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II - Application to Experimental Data

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SUMMARY

Functions, derived in a companion report (NASA TP-1929), for the representation of the thermodynamic properties of nonideal solutions have been applied to the experimental data for several highly nonideal solutions. The test solutions were selected to cover both electrolyte and nonelectrolyte behavior. The results imply that the functions are fully capable of representing the experimental data within their accuracy over the whole composition range and demonstrate that many nonideal solutions can be regarded as members of the defined class of nonideal solutions.

INTRODUCTION

A class of nonideal solutions was defined (ref. 1) by constructing a function to represent the composition dependence of thermodynamic properties for members of the class. The construction was carried out by working with the thermodynamic potential whose only extensive arguments are the composition variables. For fluids this corresponds to the Gibbs free energy treated as a function of temperature and pressure. The constructed function possesses features which are theoretically and computationally useful: (1) It reflects the known experimental behavior of dilute solutions. (2) It possesses a logarithmic singularity in the dilute solution region and contains ideal solutions and regular solutions as special cases. (3) It is directly applicable to N-ary systems and reduces to M-ary systems ($M < N$) in a form-invariant manner. (4) Its parameters, which are functions of the intensive variables, occur linearly. In this report we shall test the ability of the function to reproduce experimental thermodynamic data for real systems. That is, we shall attempt to determine to what extent real solutions can be regarded as members of the defined class of nonideal solutions. Since ideal solutions are already members of the class, it must be true that a large number of nearly ideal solutions must also be members, and thus the problem is one of determining the degree of nonideality that can be accommodated by the class. For that reason we shall confine our efforts only to highly nonideal systems, but we shall consider both nonelectrolyte and electrolyte solutions in this category.

Before we begin a discussion of the calculations, we must consider a number of questions that are relevant to the philosophy of our test and that always arise when one tries to represent experimental data by some function. Fitting a function to experimental data, based on some prescribed criteria, tests only for a consistency between function and data. We cannot separately assess the quality of the function or the data from such a test alone. Only if one or the other of these two components, the function or the data, is known to be perfect does this consistency test become a valid criterion for the evaluation of the other. Logically then, since our objective is to test the function, we should use perfect experimental data. But perfect experimental data are an unattainable ideal available only from gedanken experiments and are nonexistent in practice. Lacking perfect data we would like to have some estimate of how the real data differ from the perfect data (which we do not have). That is, we would like some estimate of the experimental error. An accurate knowledge of the experimental error could then be used to decide whether or not the function and the data are consistent within the experimental accuracy. It is illogical to require greater consistency because one is then also attempting to fit the errors in the data. To make a perfectly valid error estimate, one again needs the "true" value; but,

in practice, this is established by consensus rather than fiat and is not known when the experiments are being carried out. Consequently error estimates are just that, estimates. Unfortunately good error estimates are almost as rare as perfect experimental data, and Bridgman (ref. 2) called attention to the inherently subjective nature of such estimates with his anecdotal accounts of the measurement of the charge on the electron and Planck's constant. He pointed out that "...there seems no completely 'objective' method of estimating even the limits of error..." and that it may be "...more common for the individual investigator to overestimate the accuracy of his own measurements, but on the other hand, there are individuals who, recognizing this tendency, react by underestimating their own accuracy." This viewpoint on the subjective nature of error estimates is reinforced by Youden's account (ref. 3) of the determination of the astronomical unit, the velocity of light, and the gravitational acceleration.

Despite the clearly subjective nature of many published estimates of experimental error, it is possible to make at least a portion of the error estimate not only objective, but also experimental as was pointed out by Youden (ref. 3). Experimental error is usually assumed to have two components: random error and systematic error. The former refers to the lack of reproducibility in the experimental results which occurs without any apparent changes in the apparatus or procedure. Its contribution to the total experimental error can be estimated by adequate replication. Systematic errors are produced by some deficiency in the apparatus or the observer or may be attributable to deficiencies in the theory of the measurement. Bridgman gives a good example of how theory can drastically influence the interpretation of a measurement with his description of the effect of theoretical understanding on the experimental determination of atomic weights. Basically the design and interpretation of an experiment are often dependent on our understanding of the underlying theory which happens to be in vogue at the time the experiment is performed and a revision of our understanding could lead to a drastic reinterpretation of the experimental results. Nothing can be done to estimate systematic errors coming from this source because it represents a deficiency in our knowledge. On the other hand, Youden points out that systematic error associated with the apparatus can be estimated experimentally by constructing one or more copies of the experimental apparatus, or components of the apparatus, and comparing results from the various copies.

The examples discussed by Bridgman and Youden all concern the measurement of physical constants. The waters become substantially murkier when the experiments are measurements of functions, as they are in thermodynamics. Many more measurements must be made to define a function than a constant. Consequently replication to estimate random errors in the independent variables is the exception rather than the rule. The construction and implementation of copies of the experimental apparatus with systematic variations in components is rarer still. The clear implication is that most estimates of experimental error in thermodynamics are of the subjective variety and thus suspect and, perhaps, unreliable. Haar and Gallagher (ref. 4), in a critical evaluation of the thermodynamic properties of ammonia, conclude (p. 639) "...that estimates of quality by experimentalists are often ambiguous (and sometimes even omitted) even in work of otherwise high quality." This situation forces critical compilers of thermodynamic data to resort to procedures which, strictly speaking, can be faulted on logical grounds but which are probably unavoidable evils under current circumstances. We are referring specifically to the common practice of judging the reliability of an experimental datum point, at least in part, by its deviation from a function obtained by a preliminary fit of an equation to a set of data. This deviation

is then used to assign a weight to the point, inversely proportional to the deviation, in a subsequent fit of the data by the same or similar equation. The difficulty is that one has absolutely no assurances that the equation being used is the "correct" one. When this practice is pushed to its two logical extremes, it would allow us to conclude, at our option, that any finite set of experimental data for a function of one independent variable either (1) is well represented by a straight line or (2) is free from experimental error. The first conclusion follows if we fit the data to a straight line and assign low weights to points which deviate from the line. The second conclusion follows if we use a linear combination of linearly independent functions as the fitting function with one adjustable parameter for each datum point. This is an extreme example of what Haar and Gallagher (ref. 4, p. 437) term "overfitting," the representation of not only the general trends in the data but also the experimental error. Common sense would certainly prevent the occurrence of the two extremes but might not be adequate for intermediate situations. Practitioners of the technique are in some danger of discarding the better data and retaining the inferior. This danger clearly increases as the proportion of poor data (inaccurate but reproducible and precise) increases in a collection of data.

Often in thermodynamics there are several kinds of measurements that have a bearing on a given thermodynamic property. Each type of experiment reflects some characteristic of the dependent variable and will sample some particular region of the space of independent variables; there could be anything from complete overlap to no overlap among the regions. In such a situation one would like not only to evaluate the quality of data from a given type of experiment, but also to make some value judgment about the relative merits of data from the different types of experiments. We have already discussed just how difficult and subjective the former can be. The need for the latter only exacerbates the situation. Obviously we have no mechanism for directly comparing, and thus checking for the consistency of, data from disjoint regions of the space of independent variables; just as we cannot directly compare data from two different points. But sometimes we cannot make a direct comparison even at the same point because the experiments often measure different combinations of the dependent variable and its derivatives. The only possible comparison is an indirect one – a comparison of the data to a value calculated from a fitted equation. We have already pointed out the inherent difficulties associated with this method of evaluating the quality of data.

The importance of data consistency and its effect on the fitting of that data has been strongly emphasized by Haar and Gallagher (ref. 4, pp. 636, 637, 651, 655, and 662), who observed that data inconsistencies can drastically affect the results of the fitting even outside the region where the inconsistency occurs. They even found it desirable to use weighting functions to reduce the effect of such inconsistencies by smoothing the transition between inconsistent data sets. There are two approaches to resolving the problem of potential inconsistencies in data from different types of experiments. Both have been used in practice although neither can offer any assurances that the resulting fitted equation is a good representation of the correct function. One approach is to use all of the experimental data in the curve fitting and let the fitting compromise among the inconsistencies in the data. It represents the maximum utilization of experimental information about the dependent variable but requires a somewhat more involved fitting procedure. The alternative method uses only a portion of the data for fitting, effectively assigns zero weight to the balance, and relegates it to a consistency test between it and the fitted equation. This approach does not

make maximum use of the information contained in the experimental data, but the fitting procedure is simpler if only one type of experimental data is used. We favor the first technique and feel it to be the more conservative in the absence of reliable information about experimental error. If valid estimates of experimental error are known, then they can always be factored into the fitting process.

Our view of the experimental situation is that it is extremely difficult, if not impossible, to make a fully reliable judgment on the quality of experimental thermodynamic data from the published information. For this reason we shall try to use as much data as are relatively easily available for the systems we select and we shall assign equal weight to each point. In this sense we make no claim to either an exhaustive compilation or a critical evaluation of the data for the chosen systems; nor do we claim a definitive representation of the chosen data. Our primary objective is to assure ourselves of an adequate quantity of experimental data to test the ability of the functions to reproduce the thermodynamic behavior of highly nonideal systems over their entire composition range. For our purposes it seemed preferable to take a somewhat cursory look at several different systems rather than an intensive and critical look at one. Nonideality and data availability motivated our selection of the systems to be studied. All of our calculations were carried out with double precision arithmetic (approximately 18 significant figures), but we shall give the values of the fitted parameters to only 14 significant figures. This numerical precision may seem surprising to those unfamiliar with the numerics of fitting calculations who realize that experimental data may often be no better than three or four significant figures. Double precision arithmetic is required in linear least squares calculations because the matrices encountered in determining the parameters are often nearly singular. Furthermore once the parameters have been determined, both the truncation of parameter values and the calculation sequence used to evaluate the fitted functions from the parameters can sometimes produce detectable (but generally not serious) changes in the calculated numbers. For the calculations to be discussed in this report we have observed that six significant figures for the parameters are often, but not always, adequate. Accordingly we have chosen to tabulate the parameters to enough figures to ensure that someone could reproduce any of the numbers we quote. The least squares parameters were calculated with a multiple linear regression computer program written by Sidik (ref. 5).

Three general precepts will guide our fitting of experimental data for individual systems: (1) Use experimentally derived quantities that are related as directly as possible to the actual experimental measurements. (2) Avoid any unnecessary assumptions about the behavior of the data. (3) Do not use smoothed values, for then one is attempting to fit the smoothing function rather than the experimental data. Typically we shall indicate the quality of the overall fit with a pair of numbers. For this purpose we shall use two combinations of the residuals, $\Delta y \equiv y(\text{obs}) - y(\text{calc})$, of a property y : the standard deviation σ and the mean of the residuals $\langle \Delta y \rangle$.

$$\left. \begin{aligned} \langle \Delta y \rangle &\equiv K^{-1} \sum_{k=1}^K \Delta y_k \\ \sigma^2 &\equiv \langle (\Delta y)^2 \rangle = K^{-1} \sum_{k=1}^K (\Delta y_k)^2 \end{aligned} \right\} \quad (1)$$

We could equally well have used the standard error of the estimate in place of σ . Its definition is identical to that of σ except that K^{-1} is replaced by the reciprocal of the difference between K and the number of fitting parameters.

We shall not attempt to minimize the number of parameters on the basis of testing the standard error of estimate for a minimum because the number of parameters is of little significance when the function is used on a computer. Basically we shall only vary the number of parameters through the degree of expansion L , and L will be either 1 or 2. That is, we shall not find it necessary to go beyond two terms in the symmetric function expansion to establish the flexibility of the function we are testing. If we were concerned with minimizing the number of parameters, then we would begin with the case $L = N$ and start eliminating insignificant parameters. In any fitting calculation it is generally true that there will exist a non-null subset of calculated parameters which contributes little to the representation of the data. These parameters could be set to zero and eliminated from the least squares calculation without materially affecting the quality of fit. The least squares computer program that we used (ref. 5) incorporates a rejection algorithm which sequentially eliminates parameters. We simply feel that minimizing the number of parameters is of minimal importance for our purposes. The fact that we used and tabulated a particular number of parameters does not mean that all of them are essential for an adequate representation of the data or that they are an optimum choice from all of those available for $L = N$.

In all computations we shall use $8.31434 \text{ J-mol}^{-1}\text{-K}^{-1}$ for the universal gas constant and 4.184 J for the calorie.

NONELECTROLYTE SYSTEMS

We shall confine our interest to heat of mixing data in our examination of nonideal, nonelectrolyte systems. There are three reasons for this choice. First, heats of mixing tend to exhibit greater deviations from ideality than, for example, volume changes on mixing and hence are a more severe test of fitting functions. Second, heats of mixing are directly measurable in contrast to, say, free energies, which require the establishment of a phase equilibrium and knowledge of the free energy of one of the phases. Systematic errors in the free energy of the known phase will contribute to the systematic errors associated with the system being measured. Third, recent years have witnessed the development of the isothermal dilution calorimeter for the rapid and routine measurement of heats of mixing. In addition to ease of operation and rapidity of measurement, the apparatus seems to be capable of higher precision and greater reproducibility than other experimental methods. Consequently it is supplanting other methods of measurement and it seems to be well on the way to becoming a standard method for the measurement of the heats of mixing of liquids. All of the experimental heats of mixing which we shall process have been generated with the isothermal dilution calorimeter.

We would like to concentrate our attentions on ternary systems because they will most likely provide a more severe test of our ability to reproduce experimental behavior than do binary systems. This drastically limits our choice of systems because the adequate characterization of a ternary system requires a considerably greater number of datum points than does a binary system. It is only the advent of the isothermal dilution calorimeter which has made the acquisition of the necessary data a realistic goal. When we

speak of a ternary system we mean a system of three components (independent species) and we include all compositions for which the mole fractions x_i , $i = 1, 2, 3$, satisfy $x_1 + x_2 + x_3 = 1$. This includes compositions for which one or two of the mole fractions may be zero. We shall occasionally single out particular subsets of points from a ternary system, and we shall find it convenient to give them special names. The set of compositions for which two given mole fractions are zero obviously represents a pure species, while a set of compositions for which one particular mole fraction is always zero will be called a binary subsystem of the ternary system. The set of compositions for which no mole fraction is zero will be called the set of interior points of a ternary system.

Our reliance on data generated by the isothermal dilution calorimeter suggests that we attempt to make some approximate assessment of its overall accuracy. A crude estimate of its typical accuracy can be made by comparing results from different calorimeters for several systems, an approximation to the suggestion made by Youden.

Isothermal Dilution Calorimetry

The initial development of the calorimeter was by Van Ness and coworkers (refs. 6 to 8), but other calorimeters of the Van Ness type were subsequently constructed in rapid succession (refs. 9 to 16). We know of no experiments, of the type suggested by Youden (ref. 3), to estimate the systematic error of the calorimeter quantitatively, and we must rely on the experimenters' subjective estimates. Winterhalter and Van Ness (ref. 8, p. 191) acknowledge that it is "...difficult to arrive at an objective estimate of the accuracy..." of the calorimeter, and Murakami and Benson (ref. 11, p. 563) concur because the determination of heats of mixing "... involves a delicate balance of energies from a number of sources..." The typical experimental run with the isothermal dilution calorimeter is the successive dilution of an initial solution with a second solution. Both Murakami and Benson (ref. 11, p. 563) and Ramalho and Ruel (ref. 12, p. 457) point out that errors for successive dilutions tend to be cumulative. Murakami and Benson cite a typical "blank" experiment in which ethanol was diluted with ethanol 10 successive times. This dilution process should have had a zero heat effect, but the error in the energy for each dilution varied from zero to 0.08 J and accumulated to 0.4 J during the course of the run. Presumably this error can be either positive or negative, and thus the spread in measured values from this source alone can amount to almost a joule in a case where the experimenter knows the exact answer expected of him. Similar, and perhaps more severe, errors should be expected in an actual experiment to determine nonzero heats of mixing because heat effects are larger and the experimentalist is less likely to know the expected answer in advance.

Winterhalter and Van Ness (ref. 8, p. 191), Pflug et al. (ref. 10, p. 408), and Murakami and Benson (ref. 11, p. 571) all feel that their results are within ± 1 percent of the true values. Murakami and Benson compare an equation fitted to their data with a similar equation fitted to data from other sources for a number of binary systems. Such a comparison, while far from ideal, possibly can serve as a qualitative indicator of disparity in experimental results because of the similarity of equations in each case. They express the comparison as the root mean square percentage deviation of a given equation from their equation for the same binary system. They find, for the weakly endothermic binary system of benzene-carbon tetrachloride at 25° C, that both the function of Savini et al. (ref. 7) and the function of

Winterhalter and Van Ness (ref. 8) are uniformly lower than their function. The former has a standard deviation of 1.45 percent and the latter a standard deviation of 1.33 percent. For the strongly exothermic binary system of dichloromethane and p-dioxane at 30° C, the function of Winterhalter and Van Ness (ref. 8) is uniformly higher, with a standard deviation of about 1.35 percent and a maximum difference of about 15 J-mol⁻¹ (\approx 1.6 percent) when the mole fraction of dichloromethane is 0.75. On the other hand, Touhara et al. (ref. 15) make a similar comparison of their results with those of Murakami and Benson for the same dichloromethane and p-dioxane binary system and the identical form for the fitting functions. They calculate a standard deviation of 0.36 percent between the two functions. We have recalculated the differences between these two functions by working directly with the difference function. Our calculations differ somewhat from their figure 3, and this may indicate a loss of significance in their calculations. For example, we find that when the mole fraction of dichloromethane is 0.75, the two functions are virtually identical, differing only by 0.06 J-mol⁻¹. Their figure shows a difference of about 2 J-mol⁻¹. For mole fractions less than 0.75 the function of Touhara et al. is higher than the Murakami and Benson function, with a maximum deviation of about 8 J-mol⁻¹ (\approx 1.9 percent) occurring at a mole fraction of about 0.15. At this mole fraction the agreement between the Winterhalter and Van Ness function and the Murakami and Benson function is excellent. These comparisons and their one-sided nature, imply that experimental differences in the heat of mixing for binary solutions can easily exceed 10 J-mol⁻¹ and a percentage error of ± 1.5 percent. This assessment is consistent with that given by Ramalho and Ruel (ref. 12). For highly non-ideal binary systems they cite an average maximum error of $\pm(1$ to 2 percent) and for nearly ideal binary systems, $\pm(5$ to 6 percent).

A contributing factor to errors in heats of mixing is the experimental error in composition. Pflug et al. (ref. 10) estimate that they know mole fractions to ± 0.0005 , while Ramalho and Ruel expect an accuracy of ± 0.0008 . If these values are typical, then we should expect a spread in mole fractions from about 0.0010 to 0.0016. This error can become a significant contributor to error in the dilute solution region, where the heat of mixing changes rapidly with mole fraction. For example, if we use the Winterhalter and Van Ness representation of their data for the binary system dichloromethane - p-dioxane, then the mole fraction error could contribute about 3 to 5 J-mol⁻¹ when the mole fraction of dichloromethane is near 0.03. This represents an uncertainty in the value of the heat of mixing at this point of about $\pm(1.5$ to 2.5 percent).

Our discussion of errors in isothermal dilution calorimetry for binary systems leads us to conclude that, while ± 1 percent accuracy may occur, a more realistic estimate is probably $\pm(1$ to 2 percent). Furthermore the errors for very dilute solutions will generally be larger than the errors for concentrated solutions because of composition uncertainties. The benzene-cyclohexane binary system seems to be one for which the accuracy exceeds our estimate. Functions fitted to the data from nine different sources agree to nearly ± 0.5 percent (refs. 11 and 16).

The accuracy situation for the interior points of a ternary system is a little more involved. The reason is that the measured quantity is most directly related to a heat of mixing but the quantity of greatest interest is the excess enthalpy of the solution. The two are, of course, related. Let n represent moles per unit mass and M represent mass. Now suppose that $\tilde{n}\tilde{M}$ moles of a solution with composition \tilde{x}_i is added to $\bar{n}\bar{M}$ moles

of a solution with composition \bar{x}_i to form $(\bar{nM} + \tilde{nM})$ moles of a solution with composition x_i . If H is the molar enthalpy and ΔH is the excess molar enthalpy, then the heat of mixing per mole Q for these two solutions is defined to be

$$Q \equiv H(x) - qH(\bar{x}) - (1 - q)H(\tilde{x}) = \Delta H(x) - q \Delta H(\bar{x}) - (1 - q)\Delta H(\tilde{x}) \quad (2)$$

where $q = \bar{nM}/(\bar{nM} + \tilde{nM})$. Essentially, isothermal dilution calorimetry measures differences in this heat of mixing. If $Q^{(k)}$ is the heat of mixing for the solution formed by the k^{th} dilution, then

$$\Delta Q^{(k)} \equiv Q^{(k+1)} - Q^{(k)} = \Delta H(x^{(k+1)}) - \Delta H(x^{(k)}) - \Delta q^{(k)} [\Delta H(\bar{x}) - \Delta H(\tilde{x})]$$

where $Q^{(0)} = 0$, $q^{(0)} = 1$, and $q^{(k+1)} - q^{(k)} = \Delta q^{(k)}$. Thus

$$\sum_{j=0}^{k-1} \Delta Q^{(j)} = Q^{(k)} = \Delta H(x^{(k)}) - q^{(k)} \Delta H(\bar{x}) - [1 - q^{(k)}] \Delta H(\tilde{x})$$

$$k = 1, 2, \dots \quad (3)$$

From this formula we see that the experimental heat of mixing differences $\Delta Q(j)$ can be easily combined to obtain the heat of mixing $Q(k)$ without additional assumption. But to obtain the excess enthalpy from the experimental measurements requires $\Delta H(\bar{x})$ and $\Delta H(\tilde{x})$, the excess enthalpies of the two original solutions. If these two solutions are pure species, then $\Delta H(\bar{x}) = 0 = \Delta H(\tilde{x})$ and the heat of mixing is identical to the excess enthalpy. However, this is not always the case. Ramalho and Ruel (ref. 13), Morris et al. (ref. 17), and Shatas et al. (ref. 18) made measurements on the interior points of a ternary system by adding a pure species to a binary subsystem. The excess enthalpy for the starting binary $\Delta H(\bar{x})$ was not measured experimentally but was estimated by interpolating preexisting data for the binary. The incorporation of these values unnecessarily compromises experimental data with nonexperimental numbers. A related problem occurs for dilute binary solutions. Savini et al. (ref. 7) described a technique for making measurements on very dilute binary solutions by adding a dilute solution to a pure species. In this type of experiment one must know the excess enthalpy $\Delta H(\tilde{x})$ of the binary solution being added to the pure species.

Ternary systems present a more severe experimental challenge than binary systems. There is a sharp increase in the number of experimental measurements to be performed with a concomitant increase in the possibility for experimental error. This increase is accompanied by a relative diminution of the opportunity for experimental testing for data consistency (error). To see this, we need only realize that a fundamental difference exists between one- and two-dimensional composition spaces and that the isothermal dilution calorimeter is basically a one-dimensional instrument which is characterized by the experimental parameter q in equations (2) and (3). A given composition in a one-dimensional system can be approached from only two

directions. For any pair of starting solutions one can carry out a sequence of dilutions and then repeat the experiment with the same two solutions but with their roles reversed. Differences in results in the overlap region of composition can be taken as a measure of data inconsistency. Both Savini et al. (ref. 7, p. 43) and Pope et al. (ref. 9, p. 2666) mention experimental checks of this kind for binary systems. These internal consistency tests can also be carried out in experiments on ternary systems. In contrast to binary systems, a given composition in a ternary system can be approached from an infinite number of directions corresponding to the different one-dimensional systems passing through that point. On each one-dimensional subspace one can carry out an experimental test of the kind just mentioned, but in general this does not test for consistency among the various one-dimensional subspaces. The only effective experimental test for ternary and higher order systems is the determination of the heats of mixing around some closed path. Differences in results on any overlap portion of the path would be a measure of consistency for the closed path. This is not a convenient kind of experiment to carry out. Consequently data for interior points of ternary systems probably will tend to exhibit somewhat lower accuracy than binary system data simply because of the difficulty in performing experimental internal consistency tests. This view is consistent with the Ramalho and Ruel (ref. 13) assessment of error in ternary systems. They claim an average maximum error of $\pm(2$ to 3 percent), but generally they expect their results to be in the range $\pm(1$ to 2 percent). In the absence of direct experimental information and in view of the foregoing discussion we have concluded that ternary systems will probably exhibit errors in excess of $\pm(1$ to 2 percent).

Selection of Ternary Systems

In spite of the availability of the isothermal dilution calorimeter there are only two ternary systems with anything approaching adequate experimental coverage. These are the two highly nonideal systems acetone-chloroform-methanol and chloroform - ethanol - n-heptane whose heats of mixing were measured by Van Ness and coworkers (refs. 17 and 18). These data will be supplemented by measurements on the ethanol - n-heptane binary subsystem made by Ramalho and Ruel (ref. 12) and Van Ness, Soczek, and Kochar (ref. 19). Both Morris et al. (ref. 17) and Shatas et al. (ref. 18) combined interpolated values of binary excess enthalpies with measured heats of mixing in their tabulated excess enthalpies for the interior points without explicitly giving the values they used. Fortunately there is enough information for us to estimate their numbers and convert their tabulations back to heats of mixing. Neither Morris et al. (ref. 17) nor Shatas et al. (ref. 18) mention using a dilute binary solution as a feed solution for measuring the heats of mixing of dilute binary solutions. However, because some of their data extend to quite dilute solutions, it is possible that this was done. Lacking adequate information, we could only assume that this was not the case, and we will use the binary subsystem data as tabulated.

Our fitting of the experimental heat of mixing data will be based on equation (2) with $\Delta H(\tilde{x}) = 0$. For the molar excess enthalpy we shall use the function derived in a companion report (ref. 1, eq. (50)).

$$\Delta H(x) = \sum_{\ell=1}^L \varphi^{(\ell)}(x_i; N) \sum_{j=1}^N \sum_{k=1}^N \left[a_{jk}^{(\ell)} + b_{jk}^{(\ell)} \ln x_j \right] x_j x_k \quad (4)$$

In this function, the degree of expansion L satisfies the inequalities $1 \leq L \leq N$, and the quantities $a_{jk}^{(\ell)}$ and $b_{jk}^{(\ell)}$ are the fitting parameters. They are related to the parameters $\Delta \mu_{jk}^{(\ell)}$ and $\Delta \epsilon_{jk}^{(\ell)}$ of reference 1 in a simple way.

$$a_{jk}^{(\ell)} = \frac{-RT \frac{\partial (\Delta \mu_{jk}^{(\ell)}/RT)}{\partial \ln T}}{\quad} \quad (5)$$

$$b_{jk}^{(\ell)} = \frac{-RT \frac{\partial (\Delta \epsilon_{jk}^{(\ell)}/RT)}{\partial \ln T}}{\quad}$$

Since ΔH is the excess enthalpy, it is clear that $a_{ii}^{(1)} = 0$, $i = 1, 2, \dots, N$ (ref. 1, eq. (69) and the discussion of eq. (50)). The experimental data are expressed in joules per mole and will be used in that form.

Binary Subsystems of Chloroform – Ethanol – n-Heptane

In preparation for the fitting of the complete ternary system data to equation (4), we shall first look at the representation of the data for its three binary subsystems ethanol – n-heptane, chloroform – n-heptane, and chloroform-ethanol. We shall treat these subsystems as though they were binary systems and not subsystems of the ternary; that is, we shall use equation (4) with $N = 2$. The first of these binary systems, ethanol – n-heptane, is interesting for three reasons. First, it is a very nonideal system whose excess enthalpy is very asymmetric in composition and has an extremely steep gradient in the dilute ethanol region. Second, as with other alcohol-hydrocarbon systems, it is difficult to find a function which will represent the data accurately (refs. 12 and 18). Third, not only are there three sets of data measured for this system with the isothermal dilution calorimeter at 30° C, but two of these sets were generated in the same laboratory with the same apparatus.

Chronologically the first of these three sets of data was reported by Van Ness, Soczek, and Kochar (ref. 19) (VNSK), who observed that because of the steep gradient in the heat of mixing for mole fractions of ethanol less than 0.05, their experimental values "...for this composition range may well be less accurate than the 1 percent figure generally claimed for the calorimeter..." (p. 348). The most recent data set is that of Shatas et al. (ref. 18) (SAVN) who say (p. 407) that their data for "...ethanol – n-heptane are in exact agreement with earlier values..." from their laboratory, namely the VNSK data. Since neither mentions any alterations to the apparatus, any systematic differences in results should be ascribable to differences in starting materials or experimental technique. The third set of measurements is from Ramalho and Ruel (ref. 12) (RR), who say that their experimental data

for this system are in good agreement with the VNSK data. The three data sets represent a total of 63 points, of which 19 are VNSK, 18 are RR, and 26 are SAVN. The ethanol mole fraction intervals for the data are [0.0035, 0.9540] for VNSK, [0.0379, 0.9389] for RR, and [0.0025, 0.9968] for SAVN, and clearly the VNSK and SAVN data extend considerably farther into the dilute solution regions than the RR data. The value of the RR datum point at an ethanol mole fraction of 0.0885 is open to question. They tabulate both the excess enthalpy ΔH and the excess enthalpy divided by the product of ethanol and n-heptane mole fractions. At this composition the two values are inconsistent, and in a private communication M. J. Ruel was unable to resolve the question. Therefore we chose the value tabulated as ΔH divided by the product of mole fractions because this was in better agreement with the VNSK data in this region of composition.

We used equation (3) with $N = 2$ and $L = 1$ or $L = 2$ in our least squares fitting of the 63 experimental points. As mentioned before $a_{11}^{(1)} = 0 = a_{22}^{(1)}$ is always true. Furthermore for the $L = 2$ case we also tried to represent the data by arbitrarily imposing the condition $a_{11}^{(2)} = 0 = a_{22}^{(2)}$. Thus we actually tried fitting the data with three functions having 5, 10, and 12 adjustable, independent parameters, respectively. For each of the three functions we calculated the mean of the residuals and the standard deviation for each data set separately as well as for the set of all points. These are shown in table I and the least squares parameters are given in table II.

From a comparison of the standard deviations shown in table I we see that the five-parameter representation is clearly inferior to the other two. Furthermore a plot of its residuals shows them to exceed the apparent scatter in

TABLE I. - MEAN RESIDUALS AND STANDARD DEVIATIONS
FOR REPRESENTATION OF ETHANOL - n-HEPTANE
BINARY SYSTEM AT 30° C

	VNSK ^a	RR ^b	SAVN ^c	Total
L = 1 (5 parameters)				
Mean residual	5.706	0.117	-2.982	0.524
Standard deviation	12.239	8.649	9.049	10.057
L = 2 (10 parameters)				
Mean residual	1.637	1.125	-1.879	0.040
Standard deviation	3.377	2.516	4.685	3.764
L = 2 (12 parameters)				
Mean residual	1.778	0.885	-2.280	-0.152
Standard deviation	3.782	2.274	4.237	3.623

^aVan Ness et al. data (ref. 19).

^bRamalho and Ruel data (ref. 12).

^cShatas et al. data (ref. 18).

TABLE II. - LEAST SQUARES PARAMETERS FOR ETHANOL(1) - n-HEPTANE(2)
BINARY SYSTEM AT 30° C

	L = 1	L = 2	L = 2
$a_{12}^{(1)} = a_{21}^{(1)}$	$-0.90193912761395 \times 10^4$	$0.48157130162474 \times 10^7$	$-0.60673359952925 \times 10^5$
$b_{11}^{(1)}$	$-0.16948019835450 \times 10^5$	$0.95751994267578 \times 10^7$	$0.28210678812513 \times 10^7$
$b_{22}^{(1)}$	$-0.56900169335190 \times 10^4$	$0.96089324965820 \times 10^7$	$-0.15228158573627 \times 10^6$
$b_{12}^{(1)}$	$-0.60172454161004 \times 10^4$	$-0.11642011308670 \times 10^4$	$-0.47031657510670 \times 10^4$
$b_{21}^{(1)}$	$-0.11433140283961 \times 10^4$	$0.87848755946159 \times 10^4$	$-0.15501858683573 \times 10^4$
$a_{11}^{(2)}$	-----	0	$0.29367262721863 \times 10^7$
$a_{22}^{(2)}$	-----	0	$-0.31106627693176 \times 10^5$
$a_{12}^{(2)} = a_{21}^{(2)}$	-----	$-0.77950377552490 \times 10^7$	$0.36613717642403 \times 10^6$
$b_{11}^{(2)}$	-----	$-0.12962942709717 \times 10^8$	$-0.35077330352573 \times 10^7$
$b_{22}^{(2)}$	-----	$-0.12876246405762 \times 10^8$	$-0.98073070770264 \times 10^5$
$b_{12}^{(2)}$	-----	$-0.89511701585693 \times 10^7$	$-0.25797821737080 \times 10^7$
$b_{21}^{(2)}$	-----	$-0.89026085162354 \times 10^7$	$0.68571112137794 \times 10^5$

the experimental values. On this basis we judged the five-parameter results to be an inadequate representation of the data even though the function does reproduce the general trends of the compositionally asymmetric data quite well, as is shown in figure 1. A comparison of the mean residuals given in table I implies that systematic differences exist among the three sets of measurements, and this is borne out by plots of the residuals.

The residuals for the 10-parameter function are shown in figure 2, and those for the 12-parameter function are shown in figure 3. From these figures it is clear that there is little to choose between these two representations. Essentially, all of the residuals fall within the ± 1 percent envelope and more or less uniformly fill it for both functions. Only in the

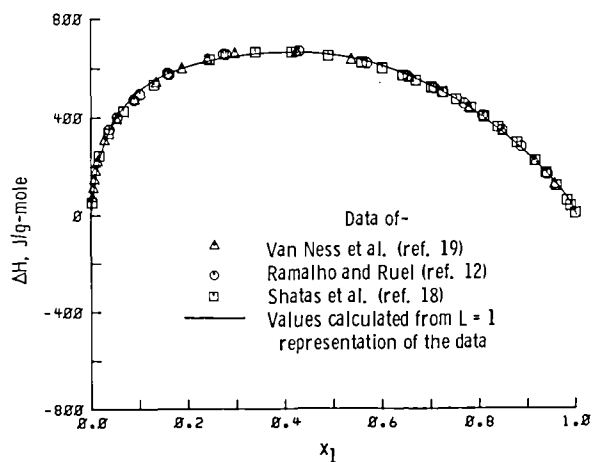


Figure 1. - Excess enthalpy of ethanol(1) - n-heptane(2) binary system at 30°C.

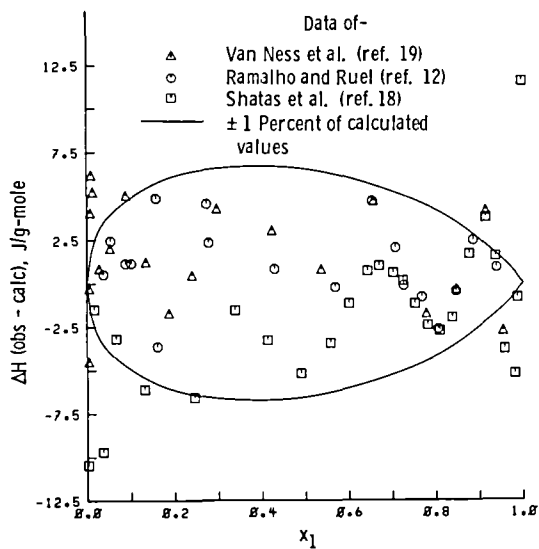


Figure 2. - Difference between observed excess enthalpy and that calculated from L = 2 representation of data with $a_{11}^{(2)} = 0 = a_{22}^{(2)}$ for ethanol(1) - n-heptane(2) binary system at 30°C.

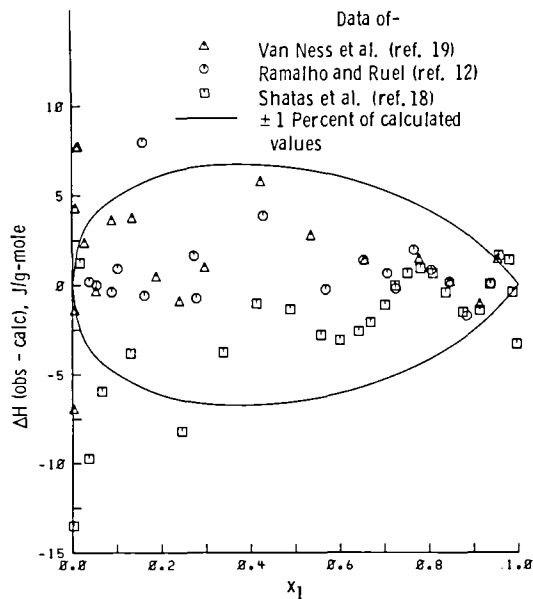


Figure 3. - Difference between observed excess enthalpy and that calculated from L = 2 representation of data for ethanol(1) - n-heptane(2) binary system at 30°C.

dilute solution regions do the points tend to fall outside the envelope, but this is consistent with our expectations, which were based on our discussion of experimental errors as well as on the evaluation of experimental difficulties in the dilute alcohol region by Morris et al. (ref. 17). There are some slight differences in the residuals in the dilute solution regions. The 10-parameter function tends to make the spread of residuals in these two regions comparable, with a value of about 15 J-mol^{-1} . The 12-parameter function reduces the spread in the ethanol-rich region to about 5 J-mol^{-1} but compensates for this by increasing the spread in the heptane-rich region to about 20 J-mol^{-1} . These figures do confirm the conjecture that systematic differences in the data sets do occur.

This is shown with greater clarity in figure 4, where the residuals for the three data sets are shown separately. The RR data generally lie between the VNSK data and the SAVN data. But the VNSK and SAVN data sets were presumably generated with the same apparatus and, if that is true, their disparity represents systematic error due to starting material and experimental technique alone. Naturally we must expect that the apparatus itself will also contribute its share to the systematic experimental error. Figure 4 also emphasizes the apparent systematic behavior of the VNSK and SAVN residuals over a large portion of the composition range, and this does not seem to be the case with the RR residuals. Systematic behavior of this nature is to be expected when one has only one nonreplicated source of data to fit but not when data come from several sources or are replicated. Indeed the systematic behavior of the two data sets is effectively masked in figure 3, where the residuals for all three data sets are depicted simultaneously. The systematicity of these residuals is therefore all the more surprising because all three sets of data were used to generate the representation and it seems to attest to cumulative errors accompanying successive dilutions in the experiment and which we discussed previously.

From figures 2, 3, and 4 it seems reasonable to conclude that equation (4) can be used to represent the data within the scatter in the experimental data and that ± 1 percent should probably be regarded as an optimistic estimate of experimental accuracy. In this connection it is interesting to note that the data of Ramalho and Ruel, who were least sanguine in their error estimates, should fall between the two data extremes.

The graphical presentation of the 10- and 12-parameter results leaves little room to doubt the ability of these functions to do justice to the experimental data. But it also seems possible to accomplish this with even fewer than 10 parameters. For example, if we use the five $\alpha = 1$ parameters together with $a_{11}^{(2)}$ and $b_{11}^{(2)}$, then these seven parameters yield a function with a standard deviation of 4.6. As we have mentioned, not all parameters are equally effective at reducing the sum of squares, and by a suitable exploration in choice of parameters it seems possible to reduce the number of parameters to fewer than seven without seriously compromising the quality of the representation. An examination of the contribution of various parameters to a reduction in the sum of squares leads us to conjecture that the five parameters $a_{11}^{(2)}$, $b_{11}^{(1)}$, $b_{11}^{(2)}$, $b_{12}^{(1)}$, and $b_{12}^{(2)}$ might be adequate for the task although we have not actually tested this combination. Regardless of what the minimum number of parameters might be or which parameters they are, it is nevertheless true that there remains a considerable amount of unused flexibility in the function (3) when representing the difficult ethanol - n-heptane binary at 30° C .

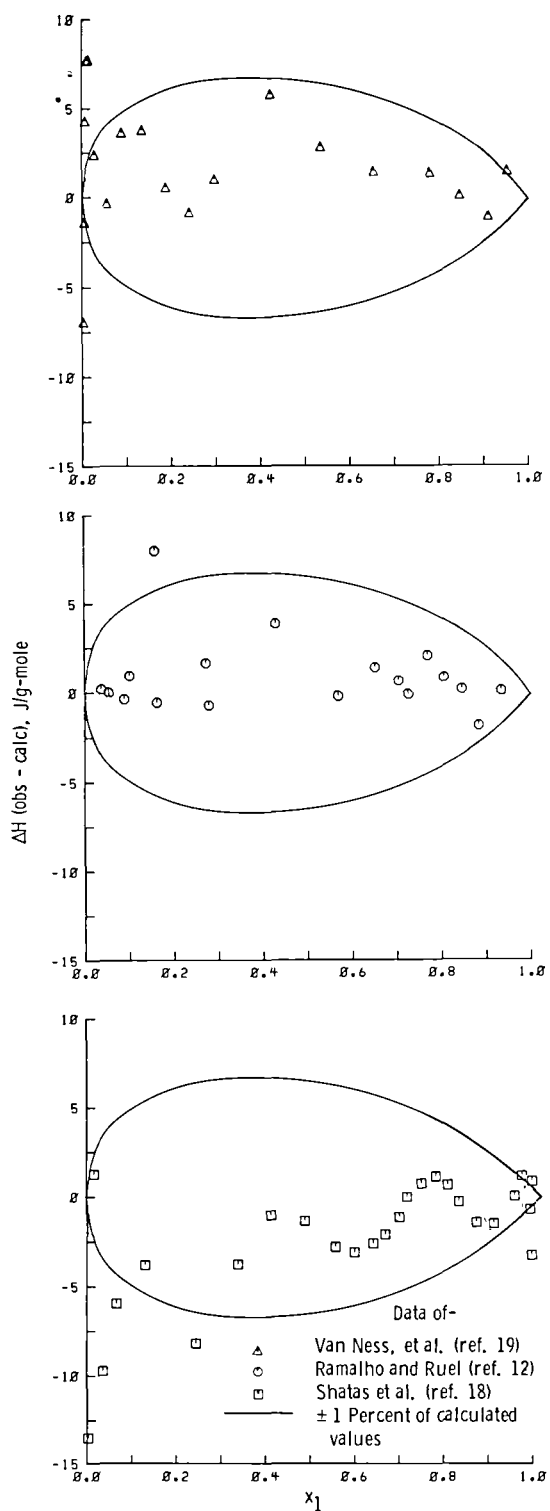


Figure 4. - Difference between observed excess enthalpy and that calculated from $L = 2$ representation of data for ethanol(1) - n-heptane(2) binary system at 30°C.

Thermodynamicists are interested not only in the properties but also in their composition derivatives, the partial molal properties. These can be calculated readily from the function (4) by using the formulas given in reference 1. The formula we need is obtained by combining equations (38), (35), and (41) of reference 1, suitably modified for the notation of equation (4) in this report. The expression for the partial molal excess enthalpy ΔH_i is

$$\Delta H_i \equiv \frac{\partial \Delta h}{\partial n_i} = \sum_{\ell=1}^L \sum_{j=1}^N x_j \left(\varphi^{(\ell)} \left[2a_{ji}^{(\ell)} + b_{ij}^{(\ell)}(1 + \ln x_i) + b_{ji}^{(\ell)} \ln x_j \right] + \sum_{k=1}^N x_k \left\{ \left[\varphi_i^{(\ell)} - (\ell + 1)\varphi^{(\ell)} \right] \left[a_{jk}^{(\ell)} + b_{jk}^{(\ell)} \ln x_j \right] - \varphi^{(\ell)} b_{jk}^{(\ell)} \right\} \right) \quad (6)$$

where Δh is the excess enthalpy per unit mass and n_i is the moles of species i per unit mass. The partial molal excess enthalpies for the ethanol - n-heptane binary system, as calculated from the 12-parameter function, are shown in figures 5 and 6 for the composition interval [0.01, 0.99]. The 10-parameter results are generally quite similar except that noticeable differences appear in the heptane partial molal excess enthalpy ΔH_2 for n-heptane mole fractions less than 0.1.

The ethanol - n-heptane binary subsystem at 30° C possessed two important characteristics: a rather complete experimental coverage of the composition range down to very dilute solutions, and three experimental data sets from the isothermal dilution calorimeter which could be used to validate our assessment of the potential systematic error magnitudes in such experiments. Neither of these two exist at 50° C, where we have only the data of Shatas et al. (ref. 18). Still it would be instructive to confirm that equation (4) can still be used to represent the SAVN data for this binary at 50° C because the data for the full ternary system are also at 50° C and we will be looking at that shortly. The parameters for the 5-parameter ($L = 1$) case and the

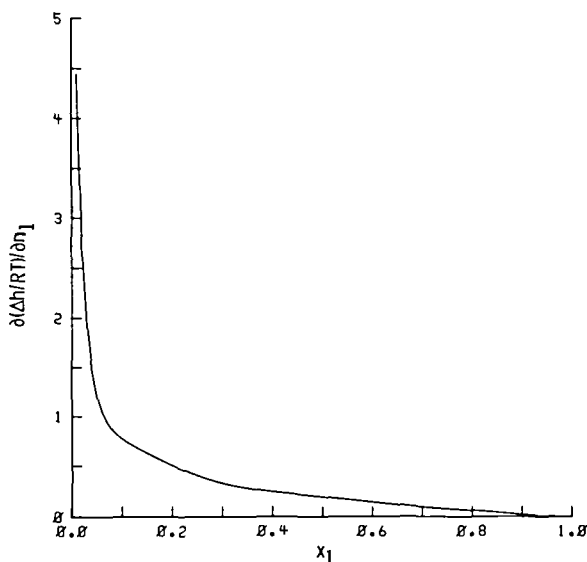


Figure 5. - Partial molal enthalpy of ethanol in ethanol(1) - n-heptane(2) binary system at 30° C as calculated from $L = 2$ representation of data.

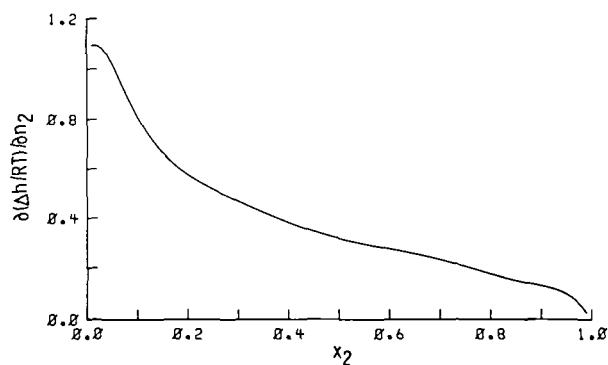


Figure 6. - Partial molal enthalpy of n-heptane in ethanol(1) - n-heptane(2) binary system at 30° C as calculated from $L = 2$ representation of data.

TABLE III. - LEAST SQUARES REPRESENTATION OF ETHANOL(1) -
n-HEPTANE(2) BINARY SYSTEM AT 50° C

	L = 2	L = 1
Mean residual	-0.065	-0.479
Standard deviation	2.393	7.186
$a_{12}^{(1)} = a_{21}^{(1)}$	$-0.15254302571297 \times 10^6$	$-0.82071100278925 \times 10^4$
$b_{11}^{(1)}$	$0.41778688955956 \times 10^7$	$-0.17880841809335 \times 10^5$
$b_{22}^{(1)}$	$-0.23282490779495 \times 10^6$	$-0.29959458007584 \times 10^4$
$b_{12}^{(1)}$	$0.26655399837606 \times 10^4$	$-0.75528423722732 \times 10^4$
$b_{21}^{(1)}$	$-0.10109307768098 \times 10^4$	$-0.64248759968319 \times 10^3$
$a_{11}^{(2)}$	$0.44809143229799 \times 10^7$	-----
$a_{22}^{(2)}$	$0.11778468153000 \times 10^6$	-----
$a_{12}^{(2)} = a_{21}^{(2)}$	$0.98607397231675 \times 10^6$	-----
$b_{11}^{(2)}$	$-0.47171017033310 \times 10^7$	-----
$b_{22}^{(2)}$	$0.77740322227478 \times 10^5$	-----
$b_{12}^{(2)}$	$-0.36164501156101 \times 10^7$	-----
$b_{21}^{(2)}$	$0.16659600957394 \times 10^6$	-----

12-parameter (L = 2) case are given in table III together with the mean residual and the standard deviation. A plot of the 5-parameter representation is shown in figure 7, and the corresponding residuals for the 33 experimental points are displayed in figure 8. Since we feel that the experimental accuracy is generally about $\pm(1$ to 2 percent) for isothermal dilution calorimetry and since the ethanol - n-heptane results at 30° C seem to be a particular corroboration of this impression, it seems reasonable to conclude that the SAVN data for ethanol - n-heptane at 50° C are represented well within their

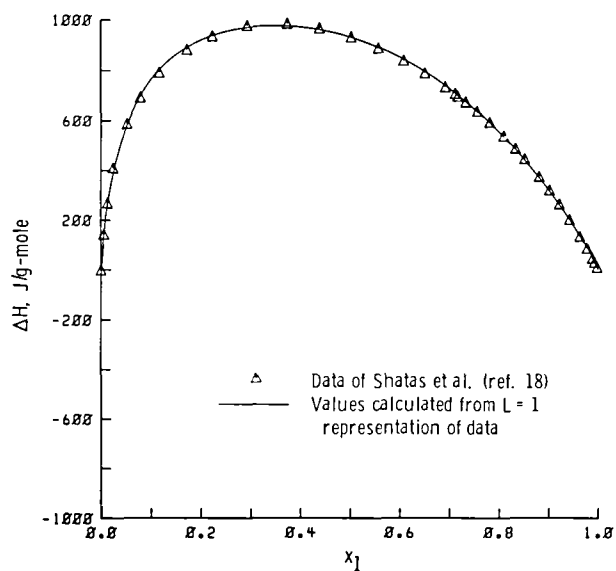


Figure 7. - Excess enthalpy of ethanol(1) - n-heptane(2) binary system at 50°C.

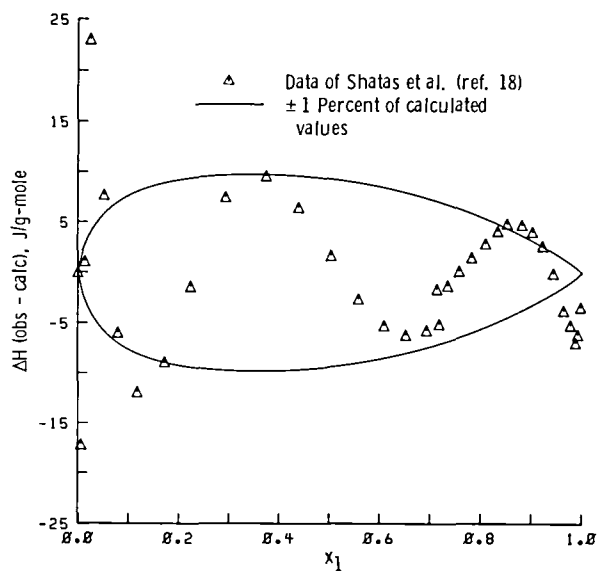


Figure 8. - Difference between observed excess enthalpy and that calculated from L = 1 representation of data for ethanol(1) - n-heptane(2) binary system at 50°C.

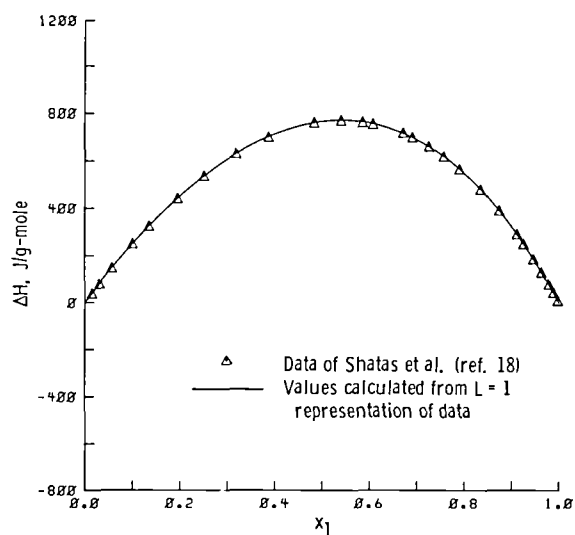


Figure 9. - Excess enthalpy of chloroform(1) - n-heptane(2) binary system at 50°C.

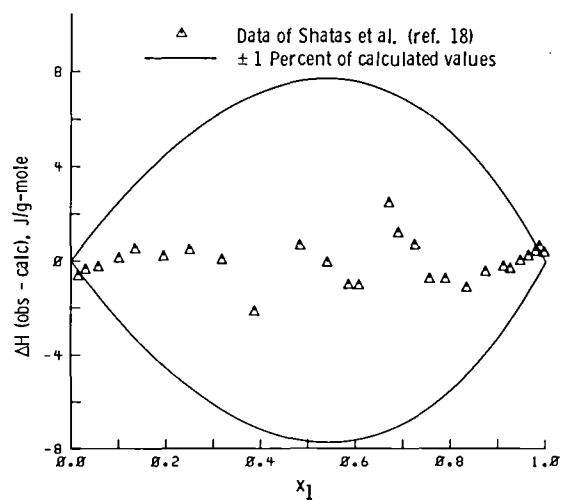


Figure 10. - Difference between observed excess enthalpy and that calculated from L = 1 representation of data for chloroform(1) - n-heptane(2) binary system at 50°C.

experimental accuracy by the 5-parameter representation. Although the 12-parameter function does give a smaller standard deviation, its use is probably not warranted because of the limited number of experimental points and their presumed accuracy. The only data overlap seems to occur at an ethanol mole fraction of about 0.71. The difference in the residuals at this composition implies that the internal consistency of the data is probably no better than about 4 J-mol⁻¹.

Like the ethanol - n-heptane binary, the chloroform - n-heptane binary at 50° C can also be represented quite well at the $L = 1$ level. This is demonstrated, for the 27 SAVN points, in figures 9 and 10. The five parameters, the mean residual, and the standard deviation are tabulated in table IV.

TABLE IV. - LEAST SQUARES REPRESENTATION
OF CHLOROFORM(1) - n-HEPTANE(2)
BINARY SYSTEM AT 50° C

	$L = 1$
Mean residual	0.022
Standard deviation	0.860
$a_{12}^{(1)} = a_{21}^{(1)}$	$0.21347163404118 \times 10^4$
$b_{11}^{(1)}$	$0.48017545322844 \times 10^2$
$b_{22}^{(1)}$	$0.16088696954520 \times 10^4$
$b_{12}^{(1)}$	$-0.25947468989983 \times 10^2$
$b_{21}^{(1)}$	$0.97057392573595 \times 10^2$

The ethanol - n-heptane and chloroform - n-heptane binaries are similar to each other because both are highly endothermic and both can be adequately represented with $L = 1$ at 50° C. The third binary pair, chloroform-ethanol, differs from the other two because it is exothermic over a portion of the composition range and endothermic over the complement of this range. Thus its excess enthalpy has an s-shaped, or sigmoid, appearance. The parameters, the mean residual, and the standard deviation for $L = 1$ and $L = 2$ obtained by fitting the 34 SAVN experimental points for the chloroform-ethanol binary are given in table V. The residuals for the 12-parameter representation are shown in figure 11, which makes it clear that they generally lie well within the ± 1 percent envelope. While the five parameters, $L = 1$, give a poorer representation of the data, the function does reproduce the general trends in the data quite well as is shown in figure 12. These chloroform-ethanol binary results are similar to the ethanol - n-heptane

TABLE V. - LEAST SQUARES REPRESENTATION OF CHLOROFORM(1) -
ETHANOL(2) BINARY SYSTEM AT 50° C

	L = 2	L = 1
Mean residual	-0.004	-0.710
Standard deviation	2.733	10.277
$a_{12}^{(1)} = a_{21}^{(1)}$	$-0.89720102187395 \times 10^5$	$-0.32246815722660 \times 10^4$
$b_{11}^{(1)}$	$-0.85956675533652 \times 10^4$	$-0.92931478046374 \times 10^4$
$b_{22}^{(1)}$	$-0.13527505103207 \times 10^6$	$0.90004329561311 \times 10^3$
$b_{12}^{(1)}$	$-0.46758294077720 \times 10^4$	$-0.51865869723518 \times 10^3$
$b_{21}^{(1)}$	$0.97235376666300 \times 10^2$	$-0.19166967241281 \times 10^4$
$a_{11}^{(2)}$	$0.18085730467272 \times 10^6$	-----
$a_{22}^{(2)}$	$0.16404075567484 \times 10^5$	-----
$a_{12}^{(2)} = a_{21}^{(2)}$	$-0.47898719527722 \times 10^5$	-----
$b_{11}^{(2)}$	$-0.31065326703584 \times 10^6$	-----
$b_{22}^{(2)}$	$0.16151375563145 \times 10^5$	-----
$b_{12}^{(2)}$	$-0.11320056806999 \times 10^6$	-----
$b_{21}^{(2)}$	$0.10606491850400 \times 10^6$	-----

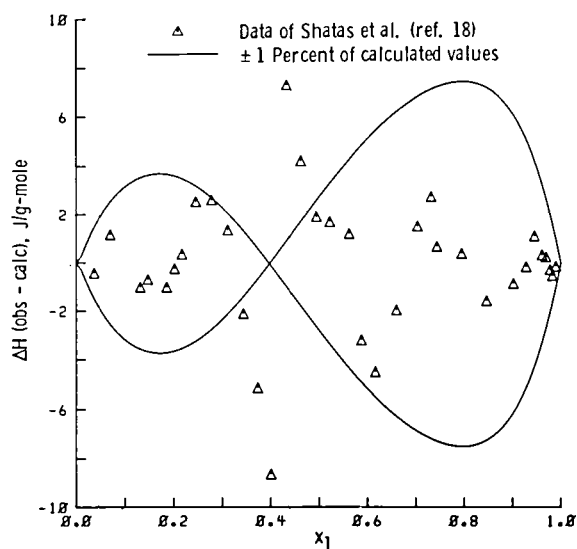


Figure 11. - Difference between observed excess enthalpy and that calculated from $L = 2$ representation of data for chloroform(1)-ethanol(2) binary system at 50° C.

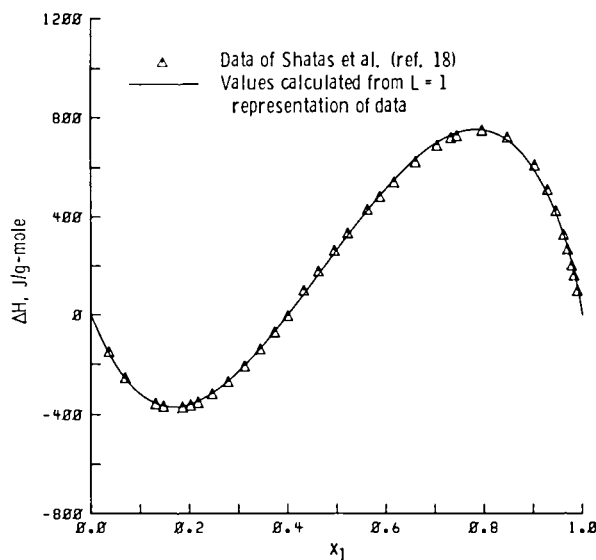


Figure 12. - Excess enthalpy of chloroform(1) - n-heptane(2) binary system at 50° C.

results at 30° C in the sense that the addition of the parameters $a_{11}^{(2)}$ and $b_{11}^{(2)}$ to the five $L = 1$ parameters improves the representation significantly. The seven parameters give a standard deviation of 3.4, not much different from the 12-parameter results. As with ethanol - n-heptane at 30° C, it seems likely that one could achieve a ± 1 percent representation of the data with five appropriately selected parameters.

Our results for the three binary subsystems suggest a reasonable conclusion: The excess enthalpies of these three very nonideal binary solutions can be represented with a precision that exceeds our estimate of experimental accuracy and even exceeds the accuracy estimates of the more optimistic experimenters. This was achieved without using the full capabilities of the functional form (3) and implies that a significant fraction of binary solutions can be regarded as members of the class of solutions defined in reference 1. We can now proceed to look at the full ternary system at 50° C.

Chloroform - Ethanol - n-Heptane Ternary System

The ternary system presents a much more difficult case for a number of reasons. We have already mentioned that a ternary system demands many more experimental measurements and that this is accompanied by an increase in the potential for internal data inconsistencies because of the two-dimensional composition space. For the particular ternary system we are now considering we have only the 284 SAVN experimental points with no corroborating experimental results from other sources which might help to judge the accuracy of the measurements. Furthermore these data offer essentially no information which might be used to establish their internal consistency. The importance of data consistency and its potential effect on the fitting of these data have been discussed earlier. Within the context of a ternary system it is possible to mitigate partially the effect of data inconsistencies by selecting a form for the fitting function which effectively produces a decoupling

among the three binary subsystems and the interior. This confines the effect of inconsistencies to each of the four subsets and prevents the interaction of inconsistencies among the four. This was the procedure used by Shatas et al. (ref. 18) and Morris et al. (ref. 17) in generating a representation of their own data. This is not an option which we permit ourselves because (1) we want a self-consistent representation of the experimental results, (2) dilute solution consistency requirements are built into the function we are testing, (3) it would be unwise to attempt to subvert these consistency requirements, which were dictated by experimental considerations, and (4) a deterioration in the representation of the binary subsystems might serve as a qualitative indicator of data inconsistencies.

As we have already mentioned, Shatas et al. (ref. 18) give their results as excess enthalpies and, for the interior points, this necessitates the use of an excess enthalpy for the initial binary solution. Table VI gives our estimates of the compositions of the initial binary mixtures as well as our estimates of the excess enthalpy values they assigned to these mixtures. We estimated the binary compositions from their tabulated compositions with an uncertainty of about 0.0001 in the mole fractions. The excess enthalpy values were calculated from these compositions and the functions they give for the least squares representation of the binary subsystems. There is some uncertainty in this calculation for the ethanol - n-heptane binary starting solutions. The reason is that when using their parameters we were unable to reproduce the standard deviation and the maximum deviation for the 50° C data in their table IV. We calculate 2.5 and 10.9, while they list 2.9 and 7.6,

TABLE VI. - ESTIMATED INITIAL BINARY
PROPERTIES FOR INTERIOR POINTS OF
CHLOROFORM(1) - ETHANOL(2) -
n-HEPTANE(3) TERNARY
SYSTEM AT 50° C

\bar{x}_1	\bar{x}_2	\bar{x}_3	$\Delta H(\bar{x}_i)$
0	0.2507	0.7493	955.4
0	0.4986	0.5014	938.0
0	0.7502	0.2498	647.7
0.0989	0	0.9011	248.0
0.2493	0	0.7507	536.7
0.4931	0	0.5069	765.6
0.7480	0	0.2520	632.9
0.8996	0	0.1004	323.8
0.0998	0.9002	0	-312.5
0.2500	0.7500	0	-317.5
0.4966	0.5034	0	263.7
0.7494	0.2506	0	732.3

for the standard deviation and the maximum deviation, respectively. This disagreement could have a number of causal factors. It might reflect a typographical error in their table. It might arise, perhaps, because they used more significant figures for their parameters than they tabulated. It might also represent numerical difficulties in their evaluation of the fitted function. Incidentally there are some minor typographical errors in the supplementary table II for the Shatas et al. (ref. 18) paper. It appears that column headings on pages 2 and 3 are interchanged and on page 3 the mole fraction 0.3814 should actually be 0.8814.

For each interior point of the SAVN data set we calculated a heat of mixing from equation (3) by using the tabulated excess enthalpies, the estimated values in table VII, and the formula

$$q = \frac{(\tilde{x}_i - x_i)}{(\tilde{x}_i - \bar{x}_i)} \quad (7)$$

where, of course, this formula can only be used for an index i such that $\tilde{x}_i - \bar{x}_i \neq 0$. These heats of mixing, together with the heats of mixing for the three binary subsystems, were then fitted in a least squares sense to equation (4) with $N = 3$ and $L = 1$ or $L = 2$. The parameters which were obtained are presented in table VII, and the standard deviation for each of the three binary subsystems, the interior points, and the complete data set are shown in table VIII. A comparison of the standard deviations for the binary subsystems with the corresponding values in tables III to V shows a considerable deterioration in the representation of the binary data. The heats of mixing for interior points are two-point functions (of \bar{x}_i and x_i or of \bar{x}_i and \tilde{x}_i) and cannot be presented graphically in a convenient way.

Consequently we only show the behavior of the representation for the binary subsystems in figures 13 to 15. The degradation of the representation is obvious and may or may not be a reflection of inconsistencies in the data. The $L = 2$ representation gives a considerably smaller standard deviation than $L = 1$, and undoubtedly $L = 3$ would show a substantial improvement over $L = 2$. We felt that it was unnecessary to carry out the $L = 3$ computation because even at $L = 2$ more than 70 percent of the heat of mixing residuals were smaller than 2 percent of the excess enthalpy. We have already expressed the opinion that the accuracy for binary solutions is about $\pm(1$ to 2 percent), and the accuracy for a ternary system is certainly no better and is probably somewhat worse. Furthermore, when we compared the $L = 2$ function obtained by fitting the heats of mixing with the $L = 2$ function obtained by fitting directly the excess enthalpies tabulated by Shatas et al., we observed differences as large as 25 J-mol^{-1} at about 23 percent of the 284 points. These differences range to more than 5 percent and often exceed 2 percent relative to the calculated excess enthalpy where they occur. These two reasons cause us to believe that the expansion of degree $L = 2$ is an adequate representation of the data. Furthermore that such a seemingly innocuous alteration of the data as the incorporation of interpolated excess enthalpies for the initial binary solutions should affect the results so strongly is a compelling argument against unnecessary pre-processing of data.

We found here, as for the binary systems, that several coefficients seem to contribute little to the reduction of the sum of squares and probably

TABLE VII. - LEAST SQUARES REPRESENTATION OF CHLOROFORM(1) - ETHANOL(2) -
n-HEPTANE(3) TERNARY SYSTEM AT 50° C

	L = 1	L = 2	
		$\ell = 1$	$\ell = 2$
$a_{11}^{(\ell)}$	0	0	$0.35911304249798 \times 10^5$
$a_{22}^{(\ell)}$	0	0	$0.51138115027874 \times 10^5$
$a_{33}^{(\ell)}$	0	0	$0.42340571347251 \times 10^5$
$a_{12}^{(\ell)} = a_{21}^{(\ell)}$	$-0.25842463839843 \times 10^4$	$-0.21899839955554 \times 10^5$	$0.38850418420850 \times 10^5$
$a_{13}^{(\ell)} = a_{31}^{(\ell)}$	$0.19550510361104 \times 10^4$	$-0.19542013566994 \times 10^5$	$0.27530508594734 \times 10^5$
$a_{23}^{(\ell)} = a_{32}^{(\ell)}$	$0.72242937269845 \times 10^3$	$-0.17950786315615 \times 10^5$	$0.47176991452899 \times 10^5$
$b_{11}^{(\ell)}$	$-0.34895056023451 \times 10^4$	$-0.13131897613996 \times 10^5$	$-0.10457265118875 \times 10^5$
$b_{22}^{(\ell)}$	$-0.33354277459552 \times 10^4$	$0.12447396929767 \times 10^5$	$-0.26441515894566 \times 10^4$
$b_{33}^{(\ell)}$	$0.47020593315850 \times 10^4$	$0.65230401766393 \times 10^4$	$-0.13409749299734 \times 10^5$
$b_{12}^{(\ell)}$	$0.13699990004981 \times 10^4$	$0.21057270183435 \times 10^3$	$0.10612166233204 \times 10^4$
$b_{21}^{(\ell)}$	$-0.35040426714391 \times 10^4$	$-0.14458961316111 \times 10^4$	$-0.13140690997225 \times 10^4$
$b_{13}^{(\ell)}$	$-0.11533465570908 \times 10^4$	$-0.14923401543861 \times 10^4$	$-0.15383362948670 \times 10^4$
$b_{31}^{(\ell)}$	$0.11223275447691 \times 10^4$	$0.16540374720901 \times 10^4$	$0.16589370133125 \times 10^3$
$b_{23}^{(\ell)}$	$-0.46049917871071 \times 10^4$	$-0.45682717303616 \times 10^4$	$0.53451399970742 \times 10^4$
$b_{32}^{(\ell)}$	$-0.71903120038646 \times 10^1$	$-0.40309672995307 \times 10^3$	$-0.32589737694593 \times 10^4$

TABLE VIII. - STANDARD DEVIATIONS FOR CHLOROFORM(1) -
ETHANOL(2) - n-HEPTANE(3) TERNARY SYSTEM AT 50° C

	Number of points	Standard deviation	
		L = 2	L = 1
1-2 Binary subsystem	34	11.985	29.131
1-3 Binary subsystem	27	12.236	21.257
2-3 Binary subsystem	33	13.899	24.662
Interior	190	10.978	20.948
Ternary system	284	11.597	21.635

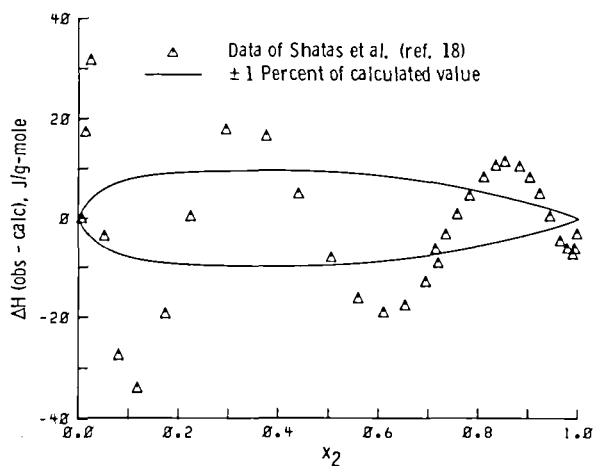


Figure 13. - Difference between observed excess enthalpy for ethanol(2) - n-heptane(3) binary subsystem at 50° C and that calculated from L = 2 representation of chloroform(1) - ethanol(2) - n-heptane(3) ternary system.

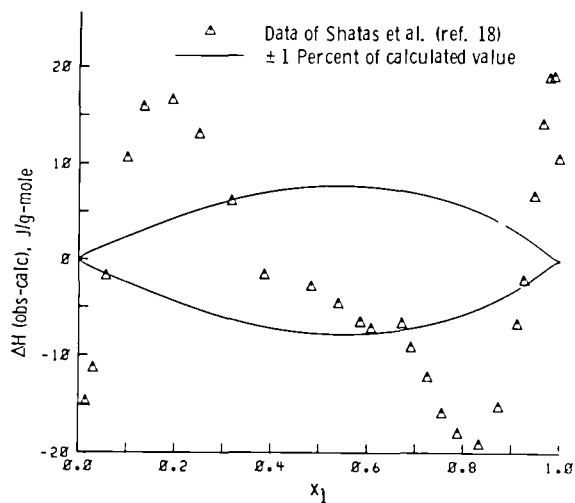


Figure 14. - Difference between observed excess enthalpy for chloroform(1) - n-heptane(3) binary subsystem at 50° C and that calculated from L = 2 representation of chloroform(1) - ethanol(2) - n-heptane(3) ternary system.

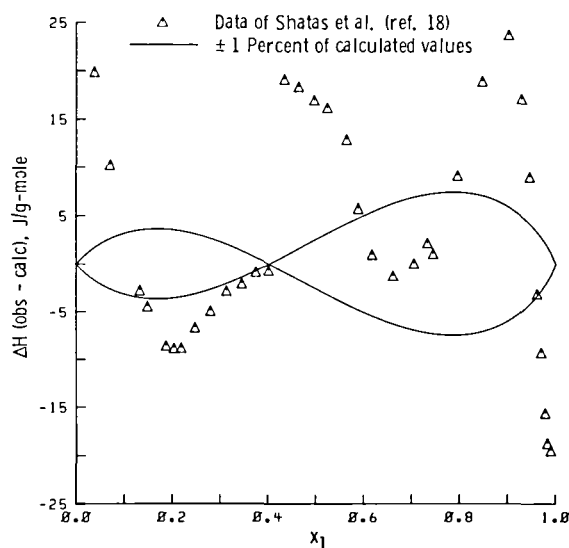


Figure 15. - Difference between observed excess enthalpy for chloroform(1)-ethanol(2) binary subsystem at 50° C and that calculated from L = 2 representation of chloroform(1) - ethanol(2) - n-heptane(3) ternary system.

could have been set to zero without seriously affecting the representation. It appears that five to seven of the coefficients for $L = 2$ make insignificant contributions to the reduction of the sum of squares.

Acetone-Chloroform-Methanol Ternary System

The situation with this ternary is much the same as what we encountered with the previous ternary system. Here we have available only the 196 points measured by Morris et al. (ref. 17) (MAVN) at 50° C and no experimental information on accuracy. However, there are overlap regions in the acetone-methanol and chloroform-methanol binary subsystems which supply a small indication of internal data consistency. Like Shatas et al., Morris et al. also tabulated the excess enthalpies for the interior points rather than the heats of mixing so that we again estimated the compositions of the initial binaries and their excess enthalpies. The estimations were made in exactly the same way as was done for the SAVN data. The results of the computation are shown in table IX, and again the compositions are uncertain to about 0.0001 in the mole fractions.

There is nothing to be learned by fitting separately the binary subsystems of the MAVN data which has not already been seen with the SAVN data. Therefore we shall proceed directly to the full ternary system. The 196 values for the heats of mixing in the MAVN data set were fitted in a least squares sense to equation (4) with $N = 3$ and $L = 1$ or $L = 2$. The parameters which were obtained are presented in table X, and the standard deviation for each of the three binary subsystems, the interior points, and the complete data set are shown in table XI. The resulting representation of the excess enthalpies and the residuals for each of the three binary subsystems are shown in figures 16 to 21. The residuals for each of the three binary systems are close to being within the ± 1 percent envelope. The overlap region for the acetone-methanol binary implies an internal consistency for this binary of about 1.5 J-mol^{-1} , while the chloroform-methanol internal consistency seems to be about 5 to 15 J-mol^{-1} . It is interesting that the

TABLE IX. - ESTIMATED INITIAL BINARY PROPERTIES FOR
 INTERIOR POINTS OF ACETONE(1)-CHLOROFORM(2)-
 METHANOL(3) TERNARY SYSTEM AT 50° C

\bar{x}_1	\bar{x}_2	\bar{x}_3	$\Delta H(\bar{x}_i)$
0	0.0491	0.9509	-175.0
0	0.2459	0.7541	-400.8
0	0.4979	0.5021	37.5
0	0.7515	0.2485	540.9
0	0.9564	0.0436	340.5
0.0501	0	0.9499	133.5
0.2465	0	0.7535	538.3
0.4894	0	0.5106	763.8
0.7586	0	0.2414	612.2
0.9435	0	0.0565	191.2
0.0404	0.9596	0	-294.9
0.2488	0.7512	0	-1438.4
0.5757	0.4243	0	-1637.9
0.7315	0.2685	0	-1187.7
0.9538	0.0462	0	-223.8

TABLE X. - LEAST SQUARES REPRESENTATION OF ACETONE(1)-CHLOROFORM(2)-METHANOL(3)
TERNARY SYSTEM AT 50° C

	L = 1	L = 2	
		$\ell = 1$	$\ell = 2$
$a_{11}^{(\ell)}$	0	0	$0.59244015075209 \times 10^4$
$a_{22}^{(\ell)}$	0	0	$0.19706059936392 \times 10^5$
$a_{33}^{(\ell)}$	0	0	$0.19444224410725 \times 10^5$
$a_{12}^{(\ell)} = a_{21}^{(\ell)}$	$-0.10087021560856 \times 10^5$	$-0.10747434960212 \times 10^5$	$0.26648927645491 \times 10^4$
$a_{13}^{(\ell)} = a_{31}^{(\ell)}$	$0.35203015761209 \times 10^3$	$-0.29158154779834 \times 10^4$	$0.86749604096030 \times 10^4$
$a_{23}^{(\ell)} = a_{32}^{(\ell)}$	$-0.45266054941606 \times 10^4$	$-0.33912068545739 \times 10^4$	$0.23567818881918 \times 10^5$
$b_{11}^{(\ell)}$	$-0.47337086341441 \times 10^4$	$-0.12471544846811 \times 10^5$	$-0.11801088277716 \times 10^5$
$b_{22}^{(\ell)}$	$-0.10549192885229 \times 10^5$	$0.68480349754155 \times 10^4$	$-0.66835571294546 \times 10^4$
$b_{33}^{(\ell)}$	$0.11819878402954 \times 10^4$	$0.14778415962434 \times 10^5$	$0.35538453417803 \times 10^4$
$b_{12}^{(\ell)}$	$0.58963234380687 \times 10^2$	$-0.14633710945783 \times 10^3$	$0.33839588721777 \times 10^4$
$b_{21}^{(\ell)}$	$-0.36001524527680 \times 10^4$	$0.44653664366542 \times 10^3$	$-0.23308223574449 \times 10^4$
$b_{13}^{(\ell)}$	$-0.86189553663543 \times 10^3$	$-0.976246324111349 \times 10^3$	$-0.12122336723957 \times 10^4$
$b_{31}^{(\ell)}$	$0.78908744027748 \times 10^3$	$0.22322652022304 \times 10^4$	$0.52424906391466 \times 10^4$
$b_{23}^{(\ell)}$	$-0.17587414570078 \times 10^4$	$0.40611160397392 \times 10^3$	$0.46890799753506 \times 10^2$
$b_{32}^{(\ell)}$	$-0.20660888667431 \times 10^4$	$-0.14418328483159 \times 10^4$	$0.52288330542341 \times 10^4$

TABLE XI. - STANDARD DEVIATIONS FOR ACETONE(1) -
CHLOROFORM(2)-METHANOL(3) TERNARY SYSTEM AT 50° C

	Number of points	Standard deviation	
		L = 2	L = 1
1-2 Binary subsystem	17	9.850	56.189
1-3 Binary subsystem	20	9.029	22.039
2-3 Binary subsystem	36	6.501	18.783
Interior	123	9.817	30.271
Ternary system	284	9.218	30.706

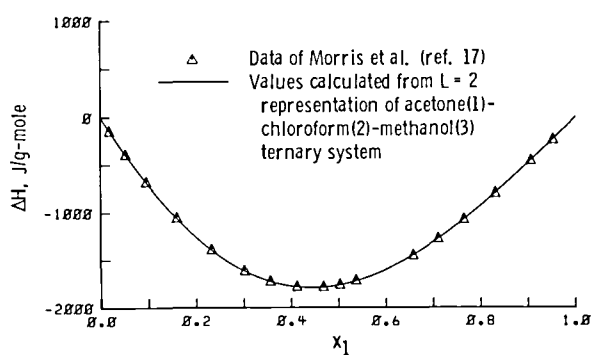


Figure 16. - Excess enthalpy for acetone(1)-chloroform(2) binary subsystem at 50° C.

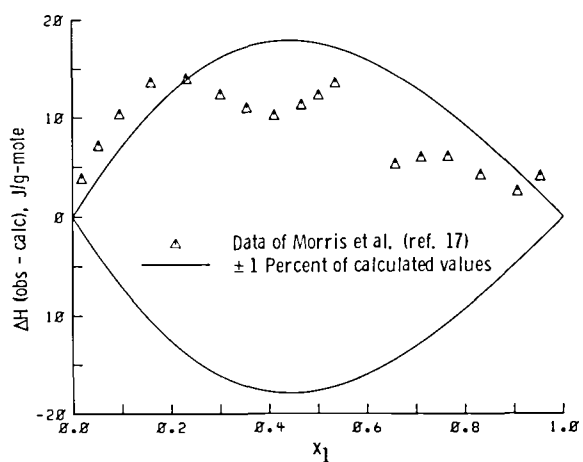


Figure 17. - Difference between observed excess enthalpy for acetone(1)-chloroform(2) binary subsystem at 50° C and that calculated from L = 2 representation of acetone(1) - chloroform(2)-methanol(3) ternary system.

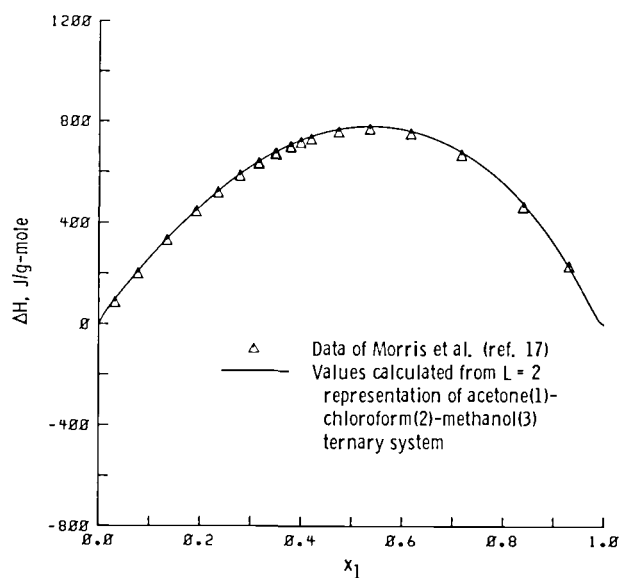


Figure 18. - Excess enthalpy for acetone(1)-methanol(3) binary subsystem at 50°C.

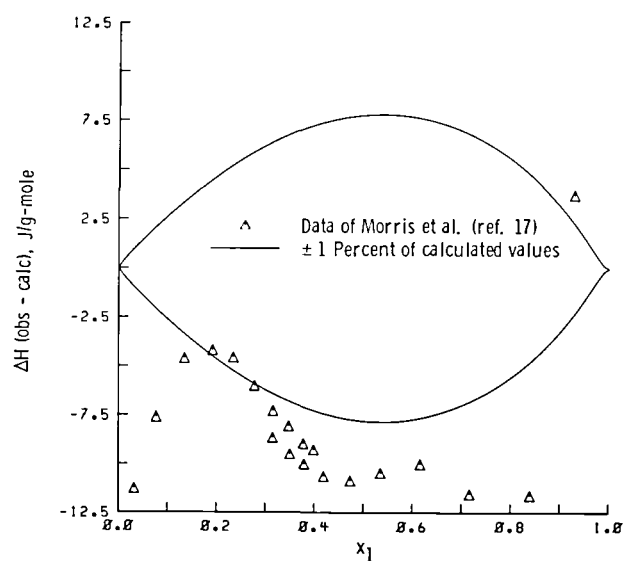


Figure 19. - Difference between observed excess enthalpy for acetone(1)-methanol(3) binary subsystem at 50°C and that calculated from L = 2 representation of acetone(1)-chloroform(2)-methanol(3) ternary system.

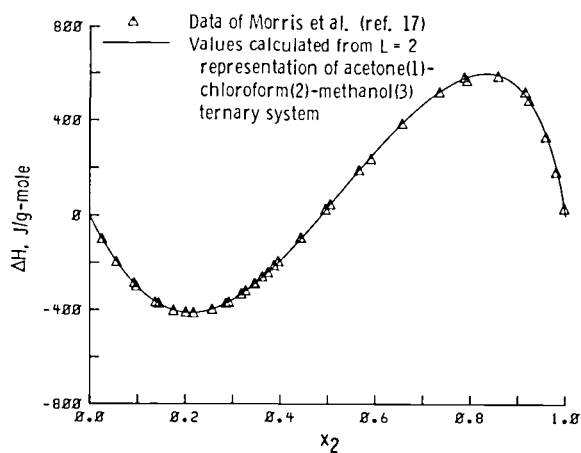


Figure 20. - Excess enthalpy for chloroform(2)-methanol(3) binary subsystem at 50°C.

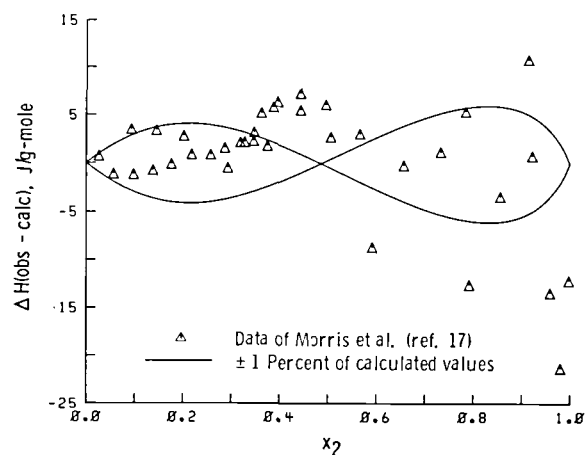


Figure 21. - Difference between observed excess enthalpy for chloroform(2)-methanol(3) binary subsystem at 50°C and that calculated from L = 2 representation of acetone(1)-chloroform(2)-methanol(3) ternary system.

residuals for the exothermic acetone-chloroform binary are all positive and the residuals for the endothermic acetone-methanol binary are, with one exception, negative. This correlation also seems to apply, with less exactitude, to the exothermic and endothermic regions of the chloroform-methanol binary. As with the SAVN data, 70 percent of the heat of mixing residuals were smaller than 2 percent of the excess enthalpy. When we compared the $L = 2$ function obtained by fitting the heats of mixing with the $L = 2$ function obtained by fitting the excess enthalpies tabulated by Morris et al., we again found differences as large as 25 J-mol^{-1} and percentage differences greater than 5 percent. However, in contrast to the results with the SAVN data, only 10 percent of the 196 points exhibited a difference of 10 J-mol^{-1} or larger. Consequently we again felt that it was unnecessary to carry out the $L = 3$ computation and that the expansion of degree $L = 2$ was an adequate representation of the system.

ELECTROLYTE SYSTEMS

We have chosen two categories of aqueous solutions of strong electrolytes to serve as test cases for the representation of experimental data by the subspace functions of reference 1. One is the two-dimensional subspace $\text{H}_2\text{O}-\text{NaCl}$ of the ternary system $\text{H}_2\text{O}-\text{Na}^+-\text{Cl}^-$, and the other is the three-dimensional subspace $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ of the quaternary system $\text{H}_2\text{O}-\text{Na}^+-\text{Ca}^{+2}-\text{Cl}^-$. These solutions were selected because (1) both are highly non-ideal and data exist over the entire concentration range from very dilute solutions to saturated solutions, (2) there are large quantities of readily available experimental data from several kinds of experiments, and (3) both are of considerable scientific and technological interest. Experimental data for these solutions have accumulated over a long time span and there seems to be a large variability in accuracy. Because the data represent such a diversity of experimental techniques, we cannot make any overall estimate of accuracy. Furthermore it would be virtually impossible to make an independent assessment of each type of measurement with any degree of assurance. As a result, we shall use the experimenters' claimed accuracy, which generally is more an estimate of reproducibility and precision than accuracy, but it should serve as a coarse indication of data quality.

We shall use 18.0154 as the formula weight for water, 58.4428 for sodium chloride, and 98.074 for calcium chloride. The energy unit will be the 4.184-J calorie because that is the unit for much of the experimental data.

$\text{H}_2\text{O}-\text{NaCl}$ Solutions

We shall focus our attention on the heats of dilution, heats of solution, and heat capacities of aqueous NaCl solutions over the temperature range 0° to 200° C and from very dilute solutions to the saturated solution. We shall use this combination of data to obtain a representation of the excess enthalpy for these solutions over the entire temperature and composition range. The stoichiometric coefficients v_{ij} for this system are given in table XII, which also gives our labeling of species. The form of the expression for the excess enthalpy is obtained from equation (65) of reference 1 and, of course, is used with $N = 3$ and $M = 2$.

TABLE XII. - STOICHIOMETRIC
COEFFICIENTS $v_{i\rho}$ FOR
AQUEOUS SODIUM CHLORIDE
SOLUTIONS

$\rho \backslash i$	H ₂ O(1)	NaCl(2)
H ₂ O(1)	1	0
Na ⁺ (2)	0	1
Cl ⁻ (3)	0	1
v_ρ	1	2

$$\left. \begin{aligned}
 \Delta H(x_\rho) &= \hat{n} n^{-1} \sum_{\ell=1}^L \varphi^{(\ell)} [x_i(x_\rho); N] \\
 &\quad \times \sum_{\sigma=1}^M \sum_{\tau=1}^M \left(a_{\sigma\tau}^{(\ell)} + \sum_{j=1}^N b_{j\tau}^{(\ell)} v_{j\sigma} \ln x_j \right) x_\sigma x_\tau \\
 \hat{n} n^{-1} &\equiv \sum_{\tau=1}^M v_\tau x_\tau \\
 x_j &\equiv \hat{n} n^{-1} \sum_{\sigma=1}^M v_{j\sigma} x_\sigma
 \end{aligned} \right\} \quad (8)$$

The heats of dilution ΔH_{dil} and the integral (or total) heats of solution ΔH_{int} in the combination $x_\sigma \Delta H_{dil}$, $x_\sigma \Delta H_{int}$, $\sigma = 2$, are just special cases of the heats of mixing, and it is these combinations which are most directly related to the measurements. They are expressible in terms of the excess enthalpies as shown in equation (3) with q calculable from the expression (7) with i replaced by $\sigma = 2$.

$$\left. \begin{aligned}
 \Delta H(x_\rho) - (x_\sigma / \bar{x}_\sigma) \Delta H(\bar{x}_\rho) &= x_\sigma \Delta H_{dil} \\
 \Delta H(x_\rho) &= x_\sigma \Delta H_{int}
 \end{aligned} \right\} \quad \sigma = 2 \quad (9)$$

Here x_ρ is the final composition and, for heats of dilution, \bar{x}_ρ is the initial composition. The excess heat capacity is the temperature derivative of the excess enthalpy.

$$\Delta C_p(x_p) = \frac{\partial \Delta H}{\partial T} \quad (10)$$

Our sources for heats of dilution were five papers (refs. 20 to 24) covering a time span of more than 50 years. The most recent data are from Messikomer and Wood (ref. 20), who reported 78 measurements at temperatures of 25°, 50°, 75°, and 100° C and initial compositions from a molality m of 5 down to 0.07. They feel that their calorimeter has an accuracy of ± 0.2 percent although the reproducibility of their measurements is considerably worse than that for small heats of dilution. The 166 points from Ensor and Anderson (ref. 21) are distributed over the temperature interval 40° to 80° C in 10 degree increments and at initial molalities from 0.07 to 6.1. Ensor and Anderson make no estimate of the accuracy of their measurements. Gulbransen and Robinson (ref. 22) made their measurements on solutions whose initial molalities were in the interval 0.006 to 0.8 and at 5 degree increments from 10° to 25° C. Their tabulated uncertainties vary with composition and temperature but typically imply that the reproducibility is about $\pm(1$ to 2 percent) although some points are less reproducible. They list 58 values. Robinson (ref. 23) provides only eight values, and these are for dilute solutions with initial molalities from 0.01 to 0.1 and at a temperature of 25° C. Again the reproducibility is generally about $\pm(1$ to 2 percent). The oldest data are the 64 points obtained by Randall and Bisson (ref. 24). We have observed what, to us, seem to be inconsistencies both in their table VII and their table IX. In table VII some of their final concentrations appear to be inconsistent with the initial concentrations based on the given initial weight of solution and the weight of the added water. Since, in many instances, the resulting solution was used as the initial solution for another dilution, these errors tend to propagate through the table. Accordingly we recalculated their compositions from the tabulated weights and accepted their value of molality for the initial solution in any given sequence of dilutions. We then calculated a heat of dilution from the composition and their value for the heat absorbed after first converting it from a 4.182 J calorie to a 4.184 J calorie. The changes in molality were usually less than 0.05 except for the first three experiments, for which the change was about 0.1. A similar inconsistency was found in their table IX; but since the compositions were determined by analysis, we accepted them and recalculated the heat of dilution from the compositions and the measured heat absorption, again converting to the 4.184 J calorie. The changes in the heat of dilution were generally less than 0.25 calorie.

The heat of solution measurements we used also cover a time interval of nearly 50 years. The more recent data are from Gardner, Mitchell, and Cobble (ref. 25) and Criss and Cobble (ref. 26). The solutions which were formed generally had molalities from about 0.002 to 0.04. The Criss and Cobble data nominally range from 0° to 95° C with 5 degree increments between 0° and 25° C and 10 degree increments between 25° and 95° C for a total of 58 points. Gardner, Mitchell, and Cobble give the results for a total of 17 measurements at 115°, 150°, and 200° C. Gardner et al. feel that their average errors (reproducibility) are approximately 25 to 50 calories. The reproducibility error of the Criss and Cobble measurements is as large as ± 73 cal/mol and as much as 10 percent of the heat of solution, but more typically it seems to be $\pm(1$ to 2 percent). The older heat of solution measurements are from Lipsett, Johnson, and Maass (refs. 27 and 28), who measured the heats of solution at 25° and 20° C. There were 20 measurements at 25° and 15 measurements at 20° C with a reproducibility of about 0.1 percent

or better for molalities greater than 0.5. For the more dilute solutions the reproducibility was somewhat worse. The solutions ranged in molality from about 0.04 to a saturated solution. Since Lipsett et al. used a 4.1825 J calorie, we converted their values to a 4.184 J calorie.

The excess heat capacity of a solution is not measured directly, but for aqueous electrolyte solutions the experiment determines the heat capacity of the solution relative to the heat capacity of the solvent, water, and this is then reported as an apparent heat capacity for the solute C_p^ϕ . The excess heat capacity can be calculated from the apparent heat capacity by using the expression

$$\Delta C_p = x_\sigma (C_p^\phi - C_\sigma^*) \quad \sigma = 2 \quad (11)$$

where C_σ^* is the constant pressure heat capacity of the pure species. Picker, Leduc, Philip, and Desnoyers (ref. 29) give 13 values of the apparent heat capacity at a nominal 24° C and molalities from 0.01 to 2. They estimated their values to be precise (reproducible?) to $\pm 3 \text{ J-mol}^{-1}\text{-K}^{-1}$ at molalities below 0.1 and to $\pm 0.5 \text{ J-mol}^{-1}\text{-K}^{-1}$ above 0.1 molal. At $m = 0.1$ the $3 \text{ J-mol}^{-1}\text{-K}^{-1}$ represents about 4 percent of the apparent heat capacity. After we had completed our calculations for this report, we learned that Desnoyers et al. (ref. 30) had discovered a systematic error in the calorimeter used by Picker et al. and had given a method to correct for the error. The effect of the correction is to lower the apparent molal heat capacities by about $3 \text{ J-mol}^{-1}\text{-K}^{-1}$ at the lower concentrations and about $2 \text{ J-mol}^{-1}\text{-K}^{-1}$ above $m = 1.0$. The corrections are about a 4 percent effect below $m = 0.4$, increasing to 13.5 percent at $m = 2$. We felt that it was not necessary to redo the calculations with the corrected data because they are only a small fraction of the total collection of data and because we are not attempting a critical evaluation of data. Randall and Rossini (ref. 31) report 19 values for the apparent heat capacity at 25° C with molalities ranging from 0.04 to 2.3. Their estimate of the error in their measurements translates into ± 0.6 percent near a molality of unity and increases for more dilute and more concentrated solutions. This becomes about ± 3 percent at a molality near 0.1. The Randall and Rossini data were converted to 4.184 J calories from 4.182 J calories. Likke and Bromley (ref. 32) reported 35 values of the specific heat at 20 degree increments between 80° and 200° C. Their claimed accuracy is ± 0.3 percent, and the molalities run from about 0.35 to 2.25. We converted these heat capacities to excess heat capacities by subtracting the mole fraction averages of the pure species heat capacities.

$$\Delta C_p = C_p - \sum_{\sigma=1}^M C_\sigma^* x_\sigma \quad (12)$$

The implementation of equations (11) and (12) requires the heat capacities of the pure species. For NaCl we used the experimental data of Leadbetter and Settatee (ref. 33) and Morrison and Patterson (ref. 34) as reported in appendix B of the paper by Baron, Leadbetter, and Morrison (ref. 35). We interpolated in the data by fitting a cubic polynomial to the data in the interval 200° to 500° C and then calculating the necessary values. For water we used the constant pressure heat capacities at saturated

TABLE XIII. - CONSTANT PRESSURE
HEAT CAPACITIES OF SODIUM
CHLORIDE AND WATER AT
SELECTED TEMPERATURES

Temperature, °C	NaCl	H ₂ O(l)
	Heat capacity, cal-K ⁻¹ -mol ⁻¹	
24.15	12.021	-----
25	12.024	-----
80	12.266	18.071
100	12.359	18.153
120	12.458	18.278
140	12.558	18.450
160	12.654	18.683
180	12.738	18.980
200	12.798	19.363

conditions which are tabulated in table 5b (p. 161) of the compilation by Schmidt (ref. 36). The specific numerical values that were used are given in table XIII.

To accommodate the temperature dependence of the data, we must make an explicit choice for the temperature dependence of the parameters in equation (8). We have no information that might guide us in making an optimum choice, and so we shall simply use cubic polynomials in temperature.

$$\left. \begin{aligned} a_{\sigma\tau}^{(\ell)}(T) &= \Delta T \left\{ (\Delta T) \left[(\Delta T) \ddot{a}_{\sigma\tau}^{(\ell)}(T_0) + \dot{\ddot{a}}_{\sigma\tau}^{(\ell)}(T_0) \right] + \dot{a}_{\sigma\tau}^{(\ell)}(T_0) \right\} + a_{\sigma\tau}^{(\ell)}(T_0) \\ b_{j\tau}^{(\ell)}(T) &= \Delta T \left\{ (\Delta T) \left[(\Delta T) \ddot{b}_{j\tau}^{(\ell)}(T_0) + \dot{\ddot{b}}_{j\tau}^{(\ell)}(T_0) \right] + \dot{b}_{j\tau}^{(\ell)}(T_0) \right\} + b_{j\tau}^{(\ell)}(T_0) \end{aligned} \right\} \quad (13)$$

where $T_0 = 298.15$ K and $\Delta T = T - T_0$. It was pointed out in reference 1, in the discussion following equation (64), that not all parameters are necessarily independent for some choices of the stoichiometric coefficients. This

TABLE XIV. - LEAST SQUARES REPRESENTATION ($L = 1$) OF EXCESS ENTHALPY
OF SODIUM CHLORIDE - WATER SOLUTIONS FROM 0° TO 200° C

	$(\Delta T)^0$	$(\Delta T)^1$	$(\Delta T)^2$	$(\Delta T)^3$
$a_{12}^{(1)}$	$-0.14361059302150 \times 10^6$	$0.25569086623065 \times 10^3$	$-0.35538881796126 \times 10^2$	$0.16426017382786 \times 10^1$
$a_{22}^{(1)}$	$0.16398786673008 \times 10^5$	$-0.15929895031918 \times 10^3$	$-0.65456734604777 \times 10^0$	$0.40788575976468 \times 10^0$
$b_{11}^{(1)}$	$-0.72386442457581 \times 10^5$	$0.13796570654814 \times 10^3$	$-0.17745389320478 \times 10^2$	$0.82106274725982 \times 10^0$
$b_{12}^{(1)}$	$-0.55192946050053 \times 10^5$	$-0.76953434443742 \times 10^2$	$-0.14641210112243 \times 10^2$	$0.99861129910465 \times 10^0$
$b_{21}^{(1)} + b_{31}^{(1)}$	$0.20095222818880 \times 10^2$	$0.16355875054598 \times 10^1$	$-0.24879763454152 \times 10^{-1}$	$0.18275207316087 \times 10^{-3}$
$b_{22}^{(1)} + b_{32}^{(1)}$	$-0.21791629597011 \times 10^4$	$0.12548934074504 \times 10^2$	$-0.19875623276575 \times 10^1$	$0.15895884520750 \times 10^{-1}$

applies to aqueous solutions of sodium chloride, where it is possible to determine only the combinations $(b_{21}^{(L)} + b_{31}^{(L)})$ and $(b_{22}^{(L)} + b_{32}^{(L)})$ rather than the four parameters separately. Of course additional conditions could always be imposed to separate them, but we shall not do so. The parameter $a_{11}^{(L)}$ must be set to zero for the excess enthalpy, but $a_{22}^{(L)}$ may be retained as a fitting parameter because pure NaCl is inaccessible from its solutions, which become saturated at a molality somewhat greater than 6.

The parameters for the $L = 1$ representation of the excess enthalpy are given in table XIV. The mean and the standard deviation of the residuals for each of the three subsets of data and for the whole data set used in the fitting are given in table XV. This table also contains the corresponding

TABLE XV. - MEAN AND STANDARD DEVIATION OF RESIDUALS FOR
L = 1 REPRESENTATION OF SODIUM CHLORIDE - WATER SOLUTIONS

	Number of points	Mean	Standard deviation
$x_2 \Delta H_{dil}$	374	0.388×10^{-2}	0.339×10^{-1}
$x_2 \Delta H_{int}$	110	$-.996 \times 10^{-3}$	$.333 \times 10^{-1}$
ΔC_p	67	$.720 \times 10^{-2}$	$.276 \times 10^{-1}$
All data	551	$.331 \times 10^{-2}$	$.331 \times 10^{-1}$
ΔH_{dil}	374	$-.879 \times 10^1$	$.253 \times 10^2$
ΔH_{int}	110	$.368 \times 10^1$	$.583 \times 10^2$

values for the heats of solution and dilution although they were not fitted directly. Since the heats of dilution are two-point functions, we shall display graphically only the heats of solution and the excess heat capabilities. Figure 22 shows the representation of the 20° and 25° C data of Lipsett et al. over the entire concentration range. The results for the Criss and Cobble measurements are shown in figure 23 and those for the Gardner et al. measurements in figure 24. The curves in the latter two figures were calculated for the exact temperatures corresponding to the data, and nominal temperatures are used only as labels. It is surprising that these low concentration values of ΔH_{int} are represented so well because the factor x_σ , $\sigma = 2$, considerably reduces their importance in the fitting process. The portrayal of the excess heat capacity is presented as figure 25; here the points labeled at 25° C are a composite of the 25° C data of Randall and Rossini and the uncorrected 24.15° C data of Picker et al. In addition to these results for the cubic temperature dependence we also performed the fitting with quadratic, linear, and constant temperature dependencies. The standard deviations for the complete data set increased in the sequence 1, 1.8, 4.3, 47 as the degree of the polynomial in temperature decreased.

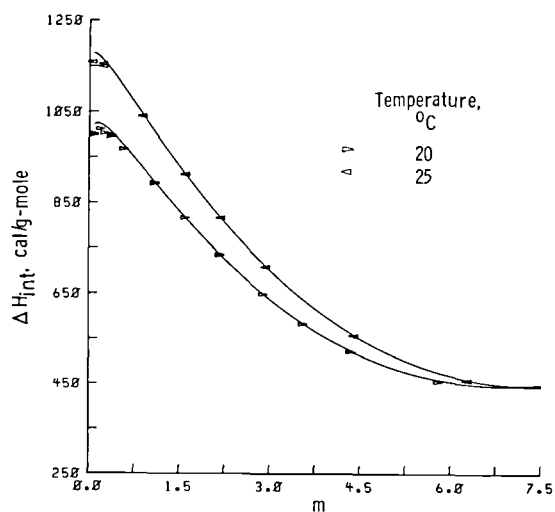


Figure 22. - Integral heat of solution of sodium chloride in water at 20° and 25° C.

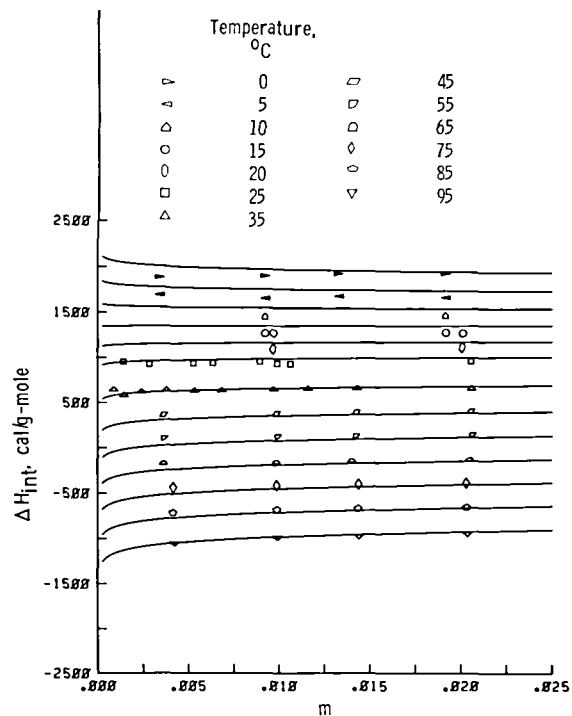


Figure 23. - Integral heat of solution of sodium chloride in water at 0°, 5°, 10°, 15°, 20°, 25°, 35°, 45°, 55°, 65°, 75°, 85°, and 95° C.

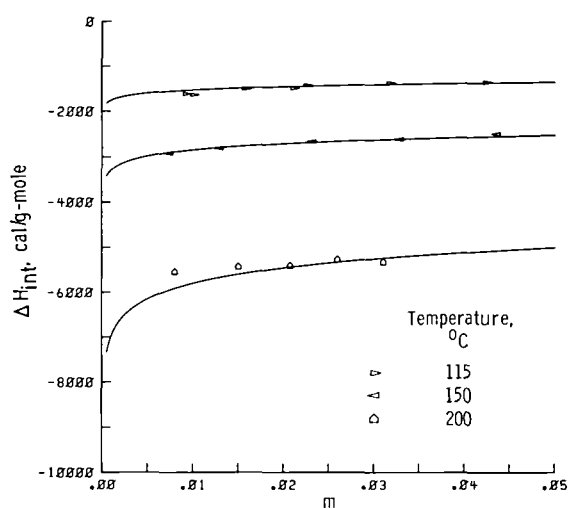


Figure 24. - Integral heat of solution of sodium chloride in water at 115°, 150°, and 200° C.

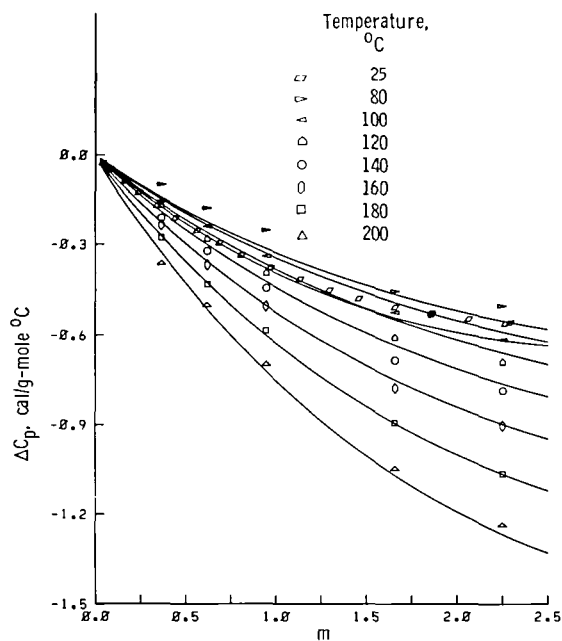


Figure 25. - Excess heat capacity of aqueous sodium chloride solutions at 25°, 80°, 100°, 120°, 140°, 160°, 180°, and 200° C.

Judging from figures 22 to 25 and the relative inaccuracy of the data as expressed by the experimenters' own estimations of random error, it seems to us that $L = 1$ gives an adequate representation of the experimental measurements. Naturally, expansions of degree $L = 2$ and $L = 3$ would reduce the standard deviation, but we feel it to be an unnecessary refinement in the present circumstances.

Statistical analysis of the reliability of least squares parameters posits that (1) random errors are independent, are normally distributed about the mean, and have an identical variance for each value of the independent variable, and (2) the variance of the normal distribution can be estimated by the square of the standard error of the estimate. It is generally conceded that the residuals are not distributed so conveniently, that is, normally with mean zero. This is easily illustrated by constructing a histogram to depict the distribution of residuals by dividing the interval $(-\infty, \infty)$ into subintervals so that the area under the normal distribution is the same for each subinterval. If the residuals are distributed in the postulated manner, then the histogram will be rectangular. The greater the deviation from rectangularity, the greater is the deviation from the postulated distribution. The least squares program we used automatically constructs such a histogram

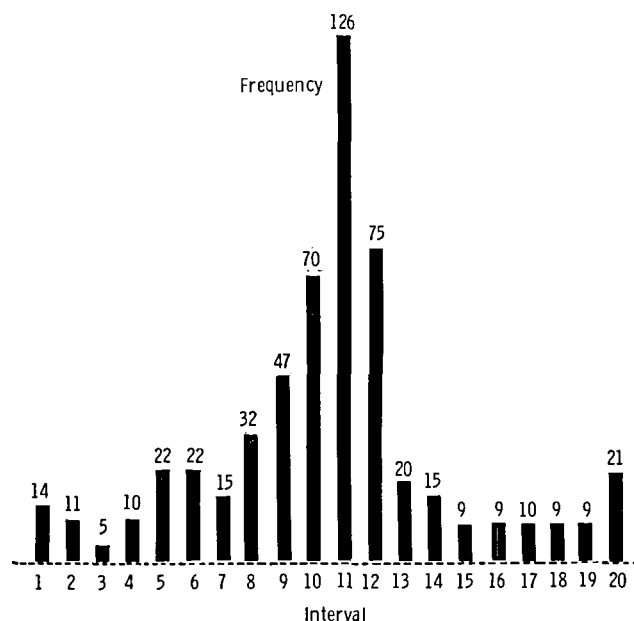


Figure 26. - Distribution of residuals from fitting of aqueous solutions of sodium chloride relative to a normal distribution of mean zero and variance equal to standard error of estimate.

with 20 subintervals, and this is shown as figure 26. The distribution of residuals diverges considerably from normal, being much more sharply peaked than the normal distribution.

H₂O-NaCl-CaCl₂ Solutions

Heretofore, we have rigorously confined ourselves in our tests to using only experimental data which were directly measurable and could be obtained without the establishment of a phase equilibrium. But now we make a complete

aqueous NaCl-CaCl₂ solutions. The value of the chemical potential is ascertained by establishing a phase equilibrium between the water vapor and the solution and by invoking the equality of chemical potentials as the condition of equilibrium. The caliber of the data is now affected not only by the quality of the measurements, but also by the extent of our knowledge of water vapor properties. Because the vapor is pure, the demands on our knowledge are not as severe as when dealing with a vapor mixture. Yet errors in vapor properties will contribute to the total error.

Our sources of information about the excess chemical potential of water in solutions at 25° C will be measurements of vapor pressure, isopiestic ratio, freezing point depression, electromotive force, and diffusion. All of these data will be combined to extract a representation of the excess chemical potential $\Delta\mu_\sigma$ for these solutions over their complete composition range. The stoichiometric coefficients and our labeling of species are given in table XVI. The expression for the excess chemical potentials is obtained by combining the first members of equations (62) to (64) of reference 1 and grouping terms. The conversion to relative quantities is done as in equation (65) of reference 1.

$$\begin{aligned} \Delta\mu_\sigma = & \sum_{\ell=1}^L \left\{ \sum_{\rho=1}^M \sum_{\tau=1}^M \left[\hat{n}n^{-1}x_\rho (2\delta_{\sigma\tau} - \hat{n}n^{-1}v_\sigma x_\tau) \varphi^{(\ell)} \right. \right. \\ & + \left. \left. (\hat{n}n^{-1})^2 \left(\varphi_\sigma^{(\ell)} - v_\sigma \varphi^{(\ell)} \right) x_\rho x_\tau \right] \Delta\mu_{\rho\tau}^{(\ell)} \right. \\ & + \sum_{i=1}^N \sum_{\tau=1}^M \left[\left(\delta_{\sigma\tau} x_i \ln x_i + \hat{n}n^{-1}x_\tau (v_{i\sigma} - x_i v_\sigma) (1 + \ln x_i) \right) \varphi^{(\ell)} \right. \\ & \left. \left. + \hat{n}n^{-1} \left(\varphi_\sigma^{(\ell)} - v_\sigma \varphi^{(\ell)} \right) x_\tau x_i \ln x_i \right] \Delta\epsilon_{i\tau}^{(\ell)} \right\} \end{aligned} \quad (14)$$

TABLE XVI. - STOICHIOMETRIC COEFFICIENTS
 $v_{i\rho}$ FOR AQUEOUS SODIUM CHLORIDE -
CALCIUM CHLORIDE SOLUTIONS

$\rho \backslash i$	H ₂ O(1)	NaCl(2)	CaCl ₂ (3)
H ₂ O(1)	1	0	0
Na ⁺ (2)	0	1	0
Ca ⁺⁺ (3)	0	0	1
Cl ⁻ (4)	0	1	2
v_ρ	1	2	3

This form of the function will be applied to data for the excess chemical potential of water at 25° C with $\sigma = 1$, $M = 3$, and $N = 4$. Much of the data will be at 25° C. However, some information for aqueous solutions of NaCl is at temperatures different from 25° C. These data will be converted to 25° C by using the expression (8) for the excess enthalpy and the least squares parameters determined for NaCl solutions tabulated in table XV. We used the formula

$$\left. \frac{\Delta\mu_{\sigma}}{RT} \right|_{T=298.15} - \frac{\Delta\mu_{\sigma}}{RT} = - \int_T^{298.15} \left(\frac{\Delta H_{\sigma}}{RT^2} \right) dT \quad (15)$$

where ΔH_{σ} is the partial molal excess enthalpy for species σ . The expression for ΔH_{σ} has a form identical to equation (14) and, of course, we shall only use the $L = 1$ part. Even though only water, and not NaCl or CaCl_2 , is accessible from aqueous solutions, we shall impose the conditions

$\Delta\mu_{\sigma\sigma}^{(1)} = 0$ for all σ . To see that the imposition of these conditions is permissible, we let ω take the fixed value $\omega = 1$. Then $v_{\omega} = 1$ and, by equations (77) and (83) of reference 1, $\mu_{\omega}^* = \mu_{\omega}^{\infty}(\omega) = \mu_{\omega\omega}^{(1)}$ and consequently we must set $\Delta\mu_{\omega\omega}^{(1)} = 0$ because we are dealing with the excess chemical

potential of water. For $\sigma \neq \omega$ we will rely on the discussion following equation (41) of reference 1. There it was shown that one could introduce a transformation of parameters such that $\mu_i = \bar{\mu}_i + \eta_i$, where the η_i are

independent of composition. Thus $\mu_{\sigma} = \bar{\mu}_{\sigma} + \eta_{\sigma}$, where $\eta_{\sigma} = \sum_{i=1}^N \eta_i v_{i\sigma}$, and

the situation here is identical to the one discussed there. That is, the values of η_{σ} , $\sigma \neq \omega$, cannot be determined from information on μ_{ω} alone and, in this context, are arbitrary. This arbitrariness permits us to use $\Delta\mu_{\sigma\sigma}^{(1)} = 0$, $\sigma \neq \omega$, and hence when we apply equation (14) to data for the excess chemical potential of water, it is permissible to set $\Delta\mu_{\sigma\sigma}^{(1)} = 0$ for all σ .

We have the option of working with the experimental data either as the excess chemical potential or as the osmotic coefficient. The relationship between the two is given in equation (92) of reference 1. When working with aqueous electrolyte solutions, the more common choice by far is the osmotic coefficient. Yet we feel this to be a poor choice for several reasons: (1) The chemical potential, and not the osmotic coefficient, is the fundamental thermodynamic quantity and for this reason alone it should be given precedence. (2) The definition of the osmotic coefficient can be viewed as a weighting of the excess chemical potential of the solvent which emphasizes the dilute solution values at the expense of the concentrated solution values. Yet, generally speaking, dilute solution measurements are the most difficult, the least reliable, and technologically the least important for there the chemical potential is essentially that of pure water. (3) The limiting value of the excess chemical potential is known exactly for it is identically zero. By contrast, the limiting value of the osmotic coefficient can never be known experimentally for, in the limit, it has the indeterminate

form 0/0 and can be evaluated only if one knows how the excess chemical potential approaches zero. But this demands the performance of the experimentally impossible task of passing to the limit. (4) Finally, as demonstrated in reference 1, we cannot even be sure that a unique limiting value exists. For all of these reasons we will shun the osmotic coefficient and favor the excess chemical potential of the solvent in our computations. Of course, we cannot avoid it entirely because the experimental results are tabulated as osmotic coefficients and must be converted to excess chemical potential values before being used.

Experimental measurements are available for sodium chloride solutions. We have decided to restrict ourselves to data obtained from vapor pressure and freezing point depression experiments. Gibbard, Scatchard, Rousseau, and Creek (ref. 37) made vapor pressure measurements for NaCl solutions whose molalities ranged from 1.0 to 6.1 and covered the temperature range 25° to 100° C. From their measurements they calculated 56 osmotic coefficients, taking vapor nonideality into account with the second virial coefficient. They did not estimate the accuracy of their osmotic coefficients, but they did give uncertainties for their pressures and temperatures. At 25° C these combine to give an uncertainty in the osmotic coefficient of almost 4 percent at a molality of 1, while at a molality of 6 the uncertainty is about 0.5 percent. At 100° C the corresponding numbers are 0.9 and 0.2 percent. Pepela and Dunlop (ref. 38) also made vapor pressure measurements for NaCl solutions but only at 25° C. The molalities extended from 0.5 to nearly 6. We corrected their 13 osmotic coefficients for vapor phase nonideality of water by using the value of $-1194 \text{ cm}^3\text{-mol}^{-1}$ for the second virial coefficient calculated from a formula given by McCullough et al. (ref. 39). The values Pepela and Dunlop claim for their uncertainties in temperature and pressure are half the values cited by Gibbard et al. The 38 vapor pressure measurements of Liu and Lindsay (ref. 40) were made at 25° C intervals from 125° to 300° C and at nominal molalities of 0.1, 0.25, 0.5, and 1.0 for NaCl. They claim that at $m = 1$ their measurements have a reproducibility which varies from about 0.2 to 0.5 percent. The reproducibility was worse at lower concentrations. Gardner (ref. 41) and Gardner, Jones, and De Nordwall (ref. 42) all made high-temperature measurements, up to 270° C, at molalities from 0.5 to 3.0. We discarded the Gardner et al. values at a molality of 1, because Gardner observed that their earlier measurements are probably low, and used the remaining 25 measurements. The final set of vapor pressure measurements are the 36 values of Olynyk and Gordon (ref. 43) at 20°, 25°, and 30° C and molalities from 2.2 to 6.1. The reproducibility of the osmotic coefficients, calculated from their tabulated values of water activity and their cited reproducibility for these activities, is better than 0.2 percent. Scatchard and Prentiss (ref. 44) give 28 values for the freezing point depression of NaCl solutions. The molalities run from very dilute solutions, $m = 0.0008$, to almost $m = 1.3$. The excess chemical potential of water at 0° C can be calculated from these data by the formula

$$\left. \frac{\Delta\mu_w}{RT} \right|_{T=273.15} = - \int_T^{273.15} \frac{(\Delta H_f + \Delta H_w)}{RT^2} dT \quad (16)$$

where ΔH_w is the partial molal excess enthalpy of water in solution and ΔH_f is the heat of fusion of pure water. We approximated the temperature dependence of the heat of fusion by a linear function of temperature, using the values $1436.3 \text{ cal-mol}^{-1}$ and $8.911 \text{ cal-mol}^{-1}\text{-C}^{-1}$ for the heat of fusion

and the heat capacity of fusion at 0° C given in National Bureau of Standards Circular 500 (ref. 45, p. 539). The values at 0° C can be converted to values at 25° C with equation (15). In actuality, we separately evaluated the integral involving the heat of fusion in equation (16) and combined the contribution of the partial molal excess enthalpy in equation (16) with the contribution arising from equation (15) in a second calculation.

The data we have discussed for aqueous NaCl solutions comprise a total of 196 experimental values for the excess chemical potential of water. We must point out that, in order to convert some of the high-temperature data to values at 25° C, we had to extrapolate our expression for the excess enthalpy of aqueous NaCl solutions. This expression was generated with data covering the temperature range 0° to 200° C.

We were fortunate to have available two recent critical evaluations of the osmotic coefficients of CaCl₂ solutions at 25° C (refs. 46 and 47) covering isopiestic, vapor pressure, freezing point depression, electromotive force, and diffusion measurements. Although both reviews called on the same sources of data, their interpretations and uses of that data differed as did some of their designations of experimental points as unreliable. The resulting two tabulations of "experimental" osmotic coefficients displayed differences as large as 0.005. These differences are a commentary on the difficulty and subjectivity of critical evaluations of data. Quite arbitrarily we chose to rely on the tabulations compiled by Rard, Habenschuss, and Spedding (ref. 46) for the osmotic coefficients at 25° C. We used directly all of their collected values with one exception. That exception was the values they give for osmotic coefficients deduced from electromotive force and diffusion measurements from 11 sources. These are relative measurements and, by quadrature of the Gibbs-Duhem equation, can give only differences in osmotic coefficients. If φ_ω is the osmotic coefficient at a molality m , φ_ω its value at \bar{m} , γ the CaCl₂ activity coefficient at m , and $\bar{\gamma}$ its value at \bar{m} , then

$$(\varphi_\omega - 1)m - (\bar{\varphi}_\omega - 1)\bar{m} = \int_{\bar{m}}^m dm' \frac{d \ln(\gamma'/\bar{\gamma})}{d \ln m'} \quad (17)$$

is the integrated Gibbs-Duhem equation. If $\bar{m} = 0$, then this can be recognized as the usual relationship connecting solute activity coefficients and osmotic coefficients. However, choosing $\bar{m} = 0$ is both an unnecessary and a nontrivial assumption for it requires the integrand to be sufficiently well behaved near zero to be integrable and necessitates an extrapolation of experimental data to zero concentration. We preferred not to set \bar{m} to zero and to determine the 11 reference values φ_ω self-consistently during the fitting. We chose our reference composition for each set of measurements as the lowest concentration in that set and evaluated the integral in equation (17) by using the representation of the integrand given by Rard et al. They compiled a total of 343 points, excluding the 11 reference values, of which 71 are from electromotive force and diffusion measurements, 20 are from vapor pressure measurements, 10 are from freezing point depression measurements, and the remaining 242 are from isopiestic experiments.

There is only limited information on aqueous solutions containing both sodium and calcium chlorides. Robinson and Bower (ref. 48) performed isopiestic experiments on mixed NaCl-CaCl₂ solutions at 25° C. They carried out equilibrations among 87 solutions, 18 containing only NaCl, 16 containing

TABLE XVII. - LEAST SQUARES REPRESENTATION OF WATER(1) - SODIUM CHLORIDE(2) -
CALCIUM CHLORIDE(3) TERNARY SYSTEM AT 25° C

	L = 1	L = 2	
		ℓ = 1	ℓ = 2
$\Delta\mu_{11}^{(\ell)}$	0	0	$-0.23448944882812 \times 10^7$
$\Delta\mu_{22}^{(\ell)}$	0	0	$0.10953599062500 \times 10^8$
$\Delta\mu_{33}^{(\ell)}$	0	0	$0.15480181218750 \times 10^8$
$\Delta\mu_{12}^{(\ell)} = \Delta\mu_{21}^{(\ell)}$	$-0.24979956572461 \times 10^6$	$0.92332410937500 \times 10^6$	$0.54690553750000 \times 10^7$
$\Delta\mu_{13}^{(\ell)} = \Delta\mu_{31}^{(\ell)}$	$-0.37146733690357 \times 10^6$	$0.21183353281250 \times 10^7$	$0.81983803750000 \times 10^7$
$\Delta\mu_{23}^{(\ell)} = \Delta\mu_{32}^{(\ell)}$	$-0.13983277311325 \times 10^4$	$0.15007752539063 \times 10^7$	$0.11720156875000 \times 10^8$
$\Delta\epsilon_{11}^{(\ell)}$	$-0.28042189677858 \times 10^6$	$-0.80329321093750 \times 10^6$	$-0.13999224062500 \times 10^7$
$\Delta\epsilon_{12}^{(\ell)}$	$-0.33988841427279 \times 10^6$	$0.17670283437500 \times 10^8$	$-0.93636997929687 \times 10^7$
$\Delta\epsilon_{13}^{(\ell)}$	$-0.56327247629261 \times 10^6$	$0.23195255140625 \times 10^8$	$-0.15101290476562 \times 10^8$
$\Delta\epsilon_{21}^{(\ell)}$	$0.12083913710937 \times 10^7$	$-0.47059946679687 \times 10^6$	$-0.16022821250000 \times 10^7$
$\Delta\epsilon_{22}^{(\ell)}$	$0.24106779765625 \times 10^7$	$0.24942743593750 \times 10^7$	$-0.11204868750000 \times 10^6$
$\Delta\epsilon_{23}^{(\ell)}$	$0.36229537421875 \times 10^7$	$0.34798746875000 \times 10^7$	$-0.52610814375000 \times 10^7$
$\Delta\epsilon_{31}^{(\ell)}$	$0.24173627617187 \times 10^7$	$-0.94181774414062 \times 10^6$	$0.14040843251953 \times 10^7$
$\Delta\epsilon_{32}^{(\ell)}$	$0.48382214687500 \times 10^7$	$-0.48254090273437 \times 10^7$	$0.36572587656250 \times 10^7$
$\Delta\epsilon_{33}^{(\ell)}$	$0.72596443281250 \times 10^7$	$-0.80189890078125 \times 10^7$	$-0.42407887500000 \times 10^6$
$\Delta\epsilon_{41}^{(\ell)}$	$-0.12072782207031 \times 10^7$	$0.47181740332031 \times 10^6$	$0.86417641875000 \times 10^7$
$\Delta\epsilon_{42}^{(\ell)}$	$-0.24097731601562 \times 10^7$	$-0.16553731250000 \times 10^8$	$0.17057722562500 \times 10^8$
$\Delta\epsilon_{43}^{(\ell)}$	$-0.35884153671875 \times 10^7$	$-0.24020932875000 \times 10^8$	$0.29762270000000 \times 10^8$

TABLE XVIII. - MEAN AND STANDARD DEVIATION OF RESIDUALS IN $\Delta\mu_w/RT$
FOR WATER - SODIUM CHLORIDE - CALCIUM SYSTEM AT 25° C

	Number of points	L = 2		L = 1	
		Mean	Standard deviation	Mean	Standard deviation
Sodium chloride	196	0.116×10^{-5}	0.387×10^{-3}	0.754×10^{-4}	0.512×10^{-3}
Calcium chloride	343	$-.184 \times 10^{-5}$	$.138 \times 10^{-2}$	$.402 \times 10^{-3}$	$.495 \times 10^{-2}$
Mixture	71	$.359 \times 10^{-4}$	$.377 \times 10^{-2}$	$-.698 \times 10^{-3}$	$.154 \times 10^{-2}$
All data	610	$.352 \times 10^{-5}$	$.106 \times 10^{-2}$	$.169 \times 10^{-3}$	$.376 \times 10^{-2}$

only CaCl_2 , and 53 containing mixed solutes. There were 10 sets of experiments, and the results were expressed as isopiestic ratios relative to NaCl . They made no estimation of the accuracy of their results. We elected to re-express their isopiestic results relative to CaCl_2 and to determine the osmotic coefficients of the 16 CaCl_2 solutions self-consistently during the fitting. Thus there are effectively 71 points.

The parameters in equation (14) were obtained in the following manner: First, we made an initial estimate of the excess chemical potential of water for the 27 reference solutions, and with these we calculated the values for those solutions which were dependent on them. The values for all 610 solutions were then fitted to equation (14) in a least squares sense, the resulting parameters were used to calculate improved estimates for the 27 reference values and the process was repeated until the calculation converged. To check on the convergence we examined the difference between the estimated and calculated values for each of the 16 reference values used with the mixture data. At convergence this difference, expressed as a difference in excess chemical potential divided by RT , was less than 7.5×10^{-8} for each of the 16 values. The corresponding difference in the 16 osmotic coefficients was less than 5×10^{-7} . Instead of using this iterative process we could have calculated the parameters directly in much the same way that we manipulated the heats of dilution for NaCl solutions. Though less efficient, we found the iterative process to be more convenient for us in the present case.

The least squares parameters, for degrees of expansion $L = 1$ and $L = 2$, are presented in table XVII. The mean residuals and the standard deviations in the excess chemical potential of water divided by RT are shown in table XVIII for the NaCl data, the CaCl_2 data, the mixture data, and for the entire data set. A comparison of the standard deviations leads us to infer that, in going from $L = 1$ to $L = 2$, the major improvement is in the representation of the CaCl_2 and mixture data. Plots of the excess chemical potential of water in aqueous NaCl and CaCl_2 solutions are shown in figures 27 and 28 for the $L = 1$ representation. Although the $L = 1$ representation is inferior to the $L = 2$ representation, it can be seen from these figures that it does represent the general trends of the data quite well. The differences between the observed and calculated values for the $L = 2$ representation are shown as figures 29 and 30. From the last two figures it is clear that the experimental data are represented within their scatter with

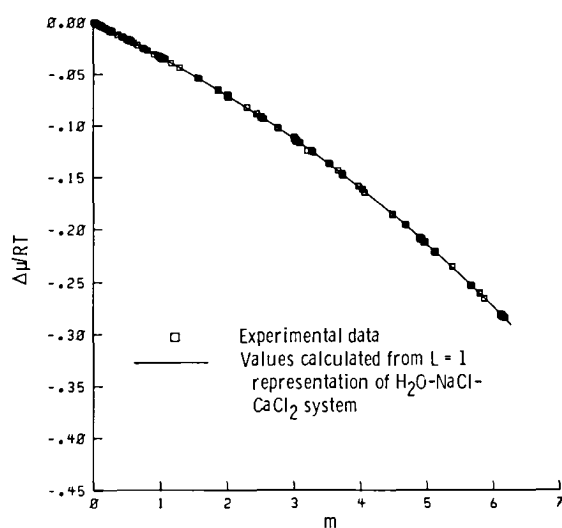


Figure 27. - Excess chemical potential of water divided by RT for aqueous sodium chloride solutions at 25°C

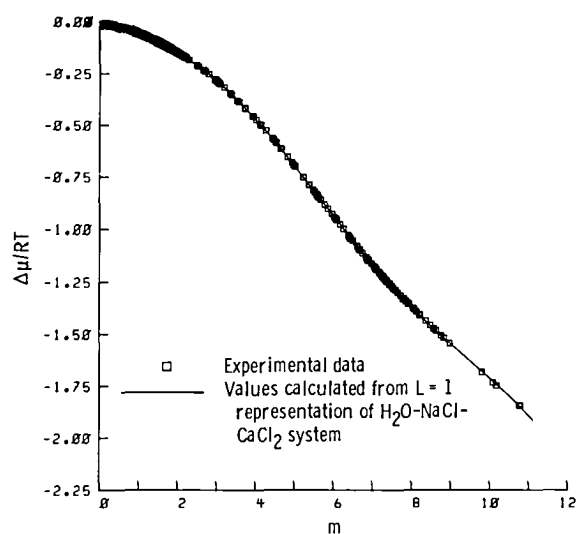


Figure 28. - Excess chemical potential of water divided by RT for aqueous calcium chloride solutions at 25°C .

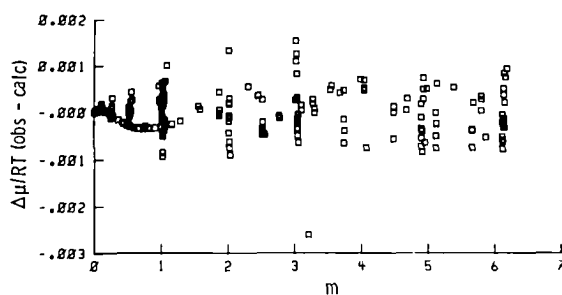


Figure 29. - Difference between observed excess chemical potential of water divided by RT for sodium chloride solutions at 25°C and values calculated from $L=2$ representation of $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ system.

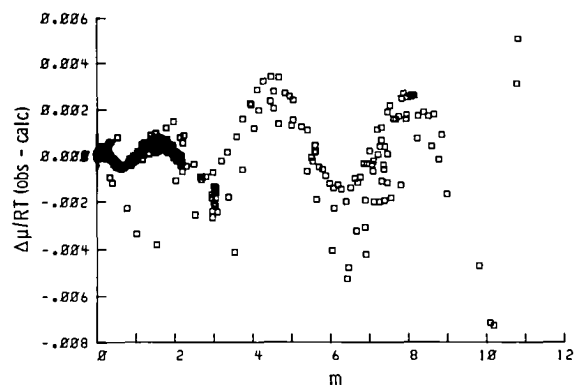


Figure 30. - Difference between observed excess chemical potential of water divided by RT for calcium chloride solutions at 25°C and values calculated from $L=2$ representation of $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ system.

$L = 2$ and that there is no reason to pursue the $L = 3$ or $L = 4$ cases. There is a marked contrast in the behavior of the NaCl and CaCl_2 residuals. The CaCl_2 residuals exhibit marked periodicities, whereas the NaCl residuals are quite random in appearance. This raises questions as to what might be the causative factors. The chief difference between the data for NaCl and CaCl_2 solutions is that for the former none of the data came from isopiestic measurements, whereas for the latter fully 2/3 of the points were isopiestic. The $L = 2$ CaCl_2 residuals have extrema at the approximate molalities 0.7, 1.6, 2.6, 4.6, 6.2, and 7.9, and in this molality range the dominant contributors of isopiestic data are Spedding et al. (ref. 49) (versus KCl reference solutions) and Rard and Spedding (ref. 50) (versus H_2SO_4 reference solutions). The residuals for these data, in the representation of the osmotic coefficient generated by Rard et al. (ref. 46), can be seen in their figure 1 and seem to have extrema at molalities near 1.0, 1.8, 2.6, 4.2, 5.6, 6.8, and 7.9. In the Staples and Nuttall representation these same data have extrema at about 0.9, 1.7, 2.2, 4.2, 5.9, and 7.4 as shown in their figure 4. The near concurrence of these extrema can hardly be regarded as coincidental especially in view of the fact that (1) three different functions were used for the representation of the data, (2) there were three different treatments of the experimental data during the fitting process, and (3) Rard et al. and Staples and Nuttall used different values for the osmotic coefficients of the reference H_2SO_4 and KCl solutions. Staples and Nuttall (p. 391) say that their H_2SO_4 reference values agree to within 0.25 percent with the values used by Rard et al., and this is less than the uncertainty in the values themselves, which seems to be between ± 0.3 percent and ± 0.5 (ref. 51, p. 379). For KCl the difference was a correction for vapor nonideality applied by Rard et al. but not by Staples and Nuttall. This correction should lower the osmotic coefficient of KCl by about 0.0014 and, indeed, CaCl_2 osmotic coefficients obtained relative to KCl are about 0.001 higher in the Staples and Nuttall tabulation than in the Rard et al. tabulation. The use of different reference values seems to implicate the isopiestic experiments as the sources of the extrema in the residuals rather than the reference values themselves although this is merely conjecture and far from a certainty. Composition uncertainties alone imply potential errors in the CaCl_2 isopiestic ratios of about ± 0.3 percent versus KCl (ref. 49) and ± 0.25 percent versus H_2SO_4 (ref. 50) values comparable to the scatter in figure 30.

The $L = 2$ representation seems to reproduce the data to within experimental uncertainties. As we have already mentioned in previous examples, if one were interested in economy of representation, one could find a number of parameters for both $L = 1$ and $L = 2$ which contribute little to the reduction of the sum of squares and could be set to zero without seriously affecting the representation.

CONCLUDING REMARKS

We have attempted to fit the thermodynamic functions of a class of non-ideal solutions, defined in a companion report (NASA TP-1929), to several different kinds of experimental data for electrolyte and nonelectrolyte solutions. All of the cases we have examined show that the functions are suitable for the representation of highly nonideal, real solutions within experimental error over their entire concentration range. Even for the highly nonideal solutions with which we have dealt, there always seemed to be unused flexibility in the function used for the fitting. This situation

happily portends the inclusion of many other nonideal solutions as members of the defined class. Only time and many more tests can show just how prevalent are the real members of this defined class.

Our tests of the composition-dependent functions have relied on the availability of copious quantities of experimental data, but that is not a prerequisite for the use of these functions. They can also be used to interpolate and extrapolate limited collections of data. As a case in point we can consider an N-ary nonelectrolyte solution. If we had only information on the properties of the $\binom{N}{2}$ binary subsystems, then we could still approximate the properties of the complete N-ary system to a degree of expansion $L = 2$. In the absence of any data whatsoever one could even rely on estimated properties generated by some approximation such as "corresponding states." Of course, the quality of the approximation will ultimately be determined by the quality and quantity of the data used to generate the approximation.

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